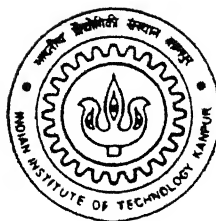


ROLE OF MANGANESE IN DESULPHURIZATION OF BLAST FURNACE METAL

by
ALOK DOBRIYAL

MME
1998
M
DOB
ROL



**DEPARTMENT OF MATERIALS & METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

JULY, 1998

ROLE OF MANGANESE IN DESULPHURIZATION OF BLAST FURNACE METAL

A Thesis Submitted

in Partial Fulfillment of the Requirements

for the Degree of

Master of Technology

by

ALOK DOBRIYAL

DEPARTMENT OF MATERIALS & METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JULY 1998

05 JAN 1999 /MME

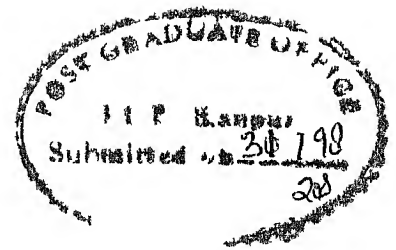
CENTRAL LIBRARY
I I T, KANPUR

~~Acc. No.~~ A 126864

MME-1998-M-DOB ROL



A126864



CERTIFICATE

It is certified that the work contained in this thesis entitled "*Role of Manganese in desulphurization of Blast Furnace metal* ", by *Alok Dobriyal*, has been carried out under my supervision and that this work has not been submitted elsewhere for any degree

Noted 30/7/98

Dr N K Batra

Professor

Materials & Metallurgical Engineering

Indian Institute of Technology

Kanpur [July, 1998]

ACKNOWLEDGEMENTS

I thank my guide, **Dr N K Batra**, for his guidance, inspiration and encouragement during the course of this project. He has taught me the values of research and independent thinking. He spent tremendous time and effort on me and was always ready to help and discuss my difficulties. It was a great pleasure working with him during the last two years.

I am also thankful to Dr S P Gupta, Dr S P Mehrotra and Dr S C Koria for their help in my project.

I must take the opportunity to thank my friends Srinu, Tanmoy, Umranikar, Raju, Maneesh, Narender and Kiety for their help in completing this thesis. I am very thankful to Shri K S Tripathi, Shri D P Tripathi and other staff members of the Institute, who helped me during my project.

Abstract

Model equations have been developed and solved using a computer to predict sulphur content of blast furnace iron with addition of manganese and iron sulphide. One silicon carbon furnace capable to reach 1400°C was designed and fabricated in the laboratory for doing experiment in the present study. Some experiments were carried out in the molybdenum disilicide raising hearth furnace at 1500°C . Results of experiment show that sulphur content decreases with an increase in manganese content of hot metal. Measured values of sulphur do not match the predicted values at 1500°C but agree well with predicted values in the temperature range of 1200 to 1300°C . Considerable drop in sulphur occurs during cooling stages.

Measured sulphur content at fixed manganese additions and with no slag addition decreases with a decrease in temperature. Results of the experiments match with predicted values using the model equations. Additions of lime bearing slag does not effect much the manganese-sulphur relation at any temperature.

CONTENTS

List of Figure

List of Tables

1	Introduction	1
1 1	Scope of present work	3
2	Literature Review	4
2 1	Activity of Sulphur in liquid iron alloy	4
2 1 1	Experimental approach to determination of thermodynamic data	4
2 1 2	Iron - Sulphur System	6
2 1 3	Iron - Carbon - Sulphur System	6
2 1 4	Effect of alloying elements on activity of sulphur	8
2 1 5	Sulphide capacity of the slag	10
2 2	Sulphur Distribution in Metal and Slag in Blast Furnace	14
2 3	Mechanism and Kinetics of Desulphurization	19
2 4	External Desulphurization of Hot Metal	25
2 5	Effect of Manganese on Desulphurization	29
3	Experimental Detail	33
3 1	Materials	33
3 2	Equipments	33
3 2 1	Super Kanthal Faising Hearth Furnace	33
3 2 2	Silicon Carbide Furnace	34
3 2 3	Digital Balance	34
3 2 4	Sulphur Analysis set-up	34
3 2 5	Photo-spectrometer	37
3 2 6	Flow-meter	37
3 3	Experimental Procedure	37
3 3 1	Master Slag Preparation	37
3 3 2	Melting of Metal and Slag Phase in Silicon carbide Furnace	37
3 3 3	Melting in Raising Hearth Furnace	38
3 4	Chemical Analysis of the Samples	38
3 4 1	Manganese determination	38

3 4 1 Sulphur determination	39
4 Thermodynamic Model for Fe-C-Mn-S System	40
4 1 Method for Interpolation of Interaction Parameters	40
4 2 Thermodynamic Model	41
5 Results and Discussion	46
6 Summary and Conclusion	58
7 References	60
8 Appendix	62
Computer Programme to Solve Model Equations	

List of Figures

2 1 Effect of sulphur concentration on K_3	7
2 2 Effect of carbon content on activity coefficient of sulphur in iron at 1600°C	9
2 3 Effect of alloying elements on activity coefficient of sulphur in iron at 1600°C	11
2 4 Correlation of sulphide capacity measurements with the empirical ratio	13
2 5 Lim/Sulphide activity coefficient ratio at 1500°C in calcium silicate melt saturated with CaS	16
2 6 Sulphur - manganese reaction equilibrium at graphite saturation and 1500°C	18
2 7 Effect of stirring on the desulphurization rate	21
2 8 Relation between mass transfer coefficients, K_m and K_s and basicity of slag	23
2 9 Concentration change of sulphur in liquid iron in slag of different basicities	24
2 10 Effect of CaF_2 percentage on desulphurization	27
2 11 Comparison of the effects of Si and Mn	28
2 12 Manganese sulphide solubility in the iron carbon melt	30
2 13 Effect of manganese on the equilibrium sulphur content of the carbon saturated melt	31
3 1 Schematic diagram of silicon carbide furnace	35
3 2 Schematic set up for sulphur analysis	36
4 1 Plot to show effect of manganese on calculated value of sulphur at the different temperature	45
5 1 Analysed manganese content of metal phase versus estimated manganese content for A category of experiments	47
5 2 Plot to show change in sulphur content with manganese addition	49
5 3 Plot to show change in equilibrium value of sulphur in the melt with temperature	51
5 4 Plot to compare the sulphur content to the melt in experiments E1 and E2 with the values predicted by the model	52

List of Tables

1 1	Typical sulphur balance in an Iron blast furnace	2
2 1	Effect of small concentration of added substances on activity coefficient of sulphur	10
2 2	Summary of methods of desulphurization	25
4 1	Lists of symbols used for material balance	43
5 1	Details of experiments carried out in the present work	53
5 2	Results of the sulphur determination in metal samples collected	54
5 3	Results of analysis of cast iron sample	56
5 4	Results of calculations of sulphur partition ratio	57

Chapter 1

INTRODUCTION

Presence of sulphur in steel is considered harmful as it lowers the mechanical properties of the steel. Low sulphur in steel is essential for getting improved notch toughness, ductility and cold pressing properties etc. and to avoid problems such as cracking and directional anisotropy encountered during hot working. If sulphur content is high, sulphur in steel gives rise to lamellar tearing in weld joints. For production of quality steel for special applications, sulphur in steel should be less than 0.01 percent. For general purpose, sulphur in steel may be in the range of 0.02 to 0.05 percent.

Main source of sulphur in steel is the blast furnace melt. Sulphur is carried into the blast furnace via raw materials in the form of iron sulphide, calcium sulphide and organic sulphides. The amount of sulphur brought in by the ore and the flux is much less compared to that brought in by the coke. Depending upon the origin, the ore and coke may contain sulphur ranging from 0.05 to 0.1 percent and 0.6 to 1.5 percent respectively. In a blast furnace, most of the sulphur is removed in the slag. Typical sulphur balance per ton of hot metal produced by the blast furnace is represented in Table 1.1.

Control of sulphur in steel should be done in the blast furnace stage itself as the extent of sulphur removal in steel making is small. Factors that control the sulphur content in the blast furnace iron include the coke rate, sulphur content of coke, slag volume and sulphur distribution ratio (α). Ignoring sulphur input via ore and fluxes and sulphur in flue gases, sulphur balance gives the following.

Table 1.1 Typical furnace sulphur balance in blast furnace for one ton of metal

Material	sulphur input kg	%	sulphur output kg	%
coke(%S) 600kg/THM	60	80		
Charge materials	1.5	20		
Iron(0.03%S)			0.3	4
Flue and dust gas			0.37	5
slag			6.82	91
Total	7.5		7.5	

$$[wt\%S] = \frac{(wt\%S)_{coke} * cokerate}{1000 + \alpha * W_{sl}} \quad (1.1)$$

where α is the sulphur partition ratio which is defined as follows

$$\alpha = \frac{(\%S)_{slag}}{[\%S]} \quad (1.2)$$

$[wt\%S]$ is the percentage of sulphur in hot metal, $(wt\%S)_{slag}$ percentage of the sulphur in the slag and W_{sl} is the amount of slag produced per ton of hot metal. Since the slag rate should be kept low for other advantages and coke rate can not be changed appreciably, low sulphur can be achieved only at high sulphur distribution ratio. High sulphur distribution ratio can be obtained by maintaining high slag basicity, high metal temperature and low Feo content of the slag.

In some cases, techno economic consideration may not justify removal of sulphur to low level either in blast furnace or in steel making. So resort is being made to a great extent to remove sulphur outside the blast furnace. The practice is known as external desulphurization of the hot metal.

1 1 **Scope of present work**

The present work involved the studies on manganese sulphur interaction in the blast furnace metal. Attempts are made to simulate conditions existing in a blast furnace as to show extent of sulphur removal with the addition of manganese with and without addition of slag of different basicity. The work involved designing and setting up of arrangements in the laboratory for studying the reactions. Theoretical calculations are made to study thermodynamics of the reactions.

Chapter 2

LITERATURE REVIEW

One of the important functions of blast furnace is control of sulphur to low levels in the hot metal before it is refined in the steel making furnace. Lot of scientific investigation on desulphurization has been done to study the slag-metal and metal-slag-gas equilibria within the blast furnace and outside the blast furnace. A comprehensive literature survey is presented in this chapter.

2.1 Activity of sulphur in liquid iron alloy

Systematic work on the distribution of sulphur between slag and metal by first finding the activity of sulphur in liquid iron base alloy was carried out by Sherman and Chipman (1).

2.1.1 Experimental approach to determination of thermodynamic data

The experiments designed to study sulphur activity were based on attainment of equilibrium between sulphur in the melt and gaseous atmosphere containing hydrogen and hydrogen sulphide. The reaction can be written as below:



$$K_1 = \frac{P_{H_2S}}{P_{H_2} a_S} \quad (2.2)$$

The standard free energy of equation (2.1) can be written as

$$\Delta G^\circ = -RT \ln K_1 \quad (2.3)$$

Equation (2.2) in the modified form can be rewritten as

$$K_2 = \frac{P_{H_2S}}{P_{H_2} f_S [\text{wt}\%S]} \quad (2.4)$$

where P_{H_2S} and P_{H_2} are the partial pressure of H_2S and H_2 respectively in the gaseous mixture and a_S represent the activity of sulphur in the melt

$$a_S = f_S [\text{wt}\%S] \quad (2.5)$$

where f_S = activity coefficient of sulphur in liquid iron

$[\text{wt}\%S]$ = percentage of sulphur in the melt

In a multicomponent system containing N solutes, f_S is given by the following equation

$$\log f_S = \sum_{j=1}^N e_S^j \text{wt}[\%j] \quad (2.6)$$

e_S^j is the henrian activity interaction parameter for 1wt% standard state. It gives effect of solute j on the activity coefficient and is defined as

$$e_S^j = \left(\frac{\partial \log f_S}{\partial \text{wt}\%j} \right)_{\text{wt}\%Fe \rightarrow 100} \quad (2.7)$$

As the concentration of solute tends to zero equation, (2.4) get modified as

$$K_2 = \left[\frac{P_{H_2S}}{P_{H_2} * [\text{wt}\%S]} \right]_{(\%wtS) \rightarrow 0} \quad (2.8)$$

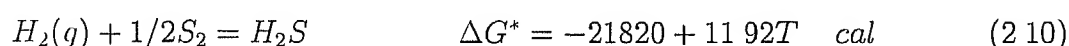
From the results of experiments of equilibrating the iron melt with certain H_2S and H_2 ratio and finding the corresponding equilibrium sulphur content of the metal, one can determine the following ratio

$$K_3 = \left[\frac{P_{H_2S}}{P_{H_2} * [\text{wt}\%S]} \right] \quad (2.9)$$

A typical plot of $(\log K_3)$ vs $[\%S]$ is shown in Fig 2.1. Value of K_2 was obtained by extrapolating the plot to zero percent sulphur. Then for any finite concentration activity coefficient of the sulphur was determined by using equation 2.4

2.1.2 Iron - Sulphur system

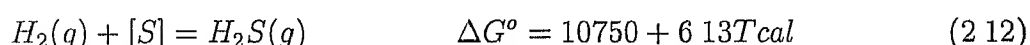
Standard free energy of formation of H_2S from gases such as H_2 and S_2 has been reported by Banya and Chipman (2) as follows



Investigators calculated the standard free energy of formation of reaction (2.10) by finding the heat and entropy of formation and reported the following

$$\Delta G^0 = -21530 + 11.37T \text{ cal} \quad (2.11)$$

They also investigated the effect of sulphur in liquid iron at $1600^\circ C$ by studying the gas-metal equilibrium and obtained the data below



Combining (2.11) and (2.12) one may get

$$1/2S_2(g) = [S] \quad \Delta G^0 = -32280 + 5.60T \text{ cal} \quad (2.13)$$

Activity coefficient f_S was reported to vary with sulphur content of iron at $1600^\circ C$ as follows,

$$\log f_S = -0.0282[wt\%S] \quad (2.14)$$

This gives value of interaction parameter as below;

$$e_s^s = -0.0282 \quad (2.15)$$

2.1.3 Iron - Carbon - Sulphur System

Carbon has pronounced effect on the activity of sulphur in the melt. Morris and Bhel (3) studied the solubility of sulphur in the iron-carbon alloy by equilibrating the melt with

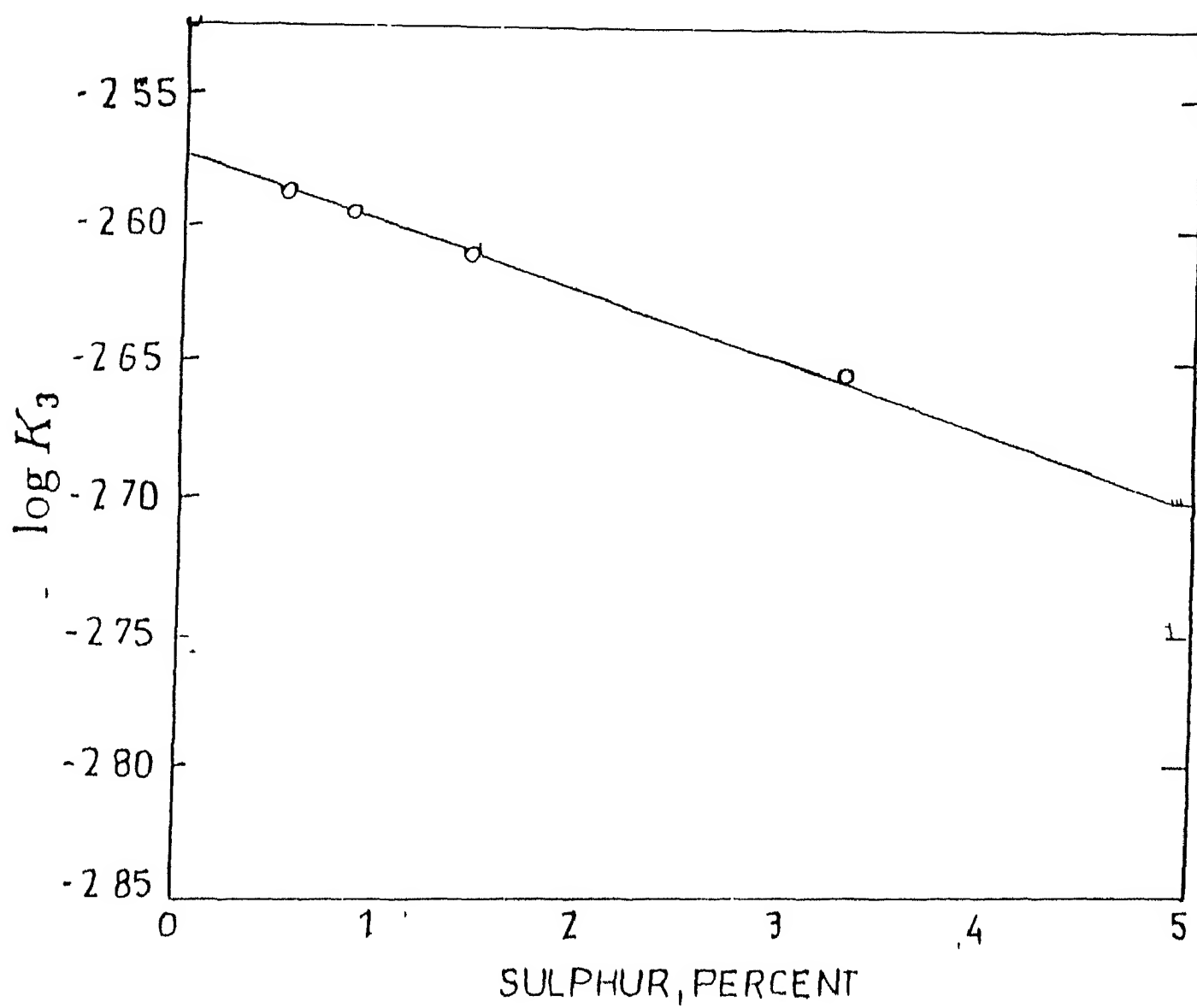
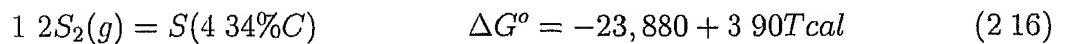


Figure 2.1 Effect of sulphur concentration on K_3

$H_2 - H_2S$ gas mixture. Then results are given in Fig 2.2

From the figure it is clear that there is an increase in the activity of sulphur in the melt. They found that the interaction parameter, e_s^C (which is the slope of $\log f_s$ vs $wt\%C$) have a value of 0.12 in the concentration range of 1-2 wt pct carbon. For carbon concentration beyond 2 pct, $\log f_s$ vs $[wt\%C]$ plot is nonlinear and equation 2.7 can not be applied directly to find e_s^s value. The slope of $\log f_s$ vs $[wt\%C]$ plot is around 0.24 when the carbon concentration was in the range of 4 to 5 wt pct. This value is sometime taken as interaction parameter for the carbon saturated solutions.

It was proposed by them that to find value of f_s accurately for a carbon saturated solution, it is desirable to use 4.35 pct carbon in iron as standard state. The free energy for the new standard state is obtained as follows



Equation (2.13) is related to equation (2.16) by the following relation

$$\Delta G^\circ_{4.35} = \Delta G^\circ + RT \ln f_s(4.35\%C) \quad (2.17)$$

f_s value has been reported as 4.2 at $1600^\circ C$ for a carbon concentration of 4.35%. Since the slope of a carbon $\log f_s$ vs $[wt\%C]$ plot is 0.24 at this carbon level, f_s at any other carbon level can be determined as follows

$$\log f_s^c = \log 4.2 + 0.24(X - 4.35) \quad (2.18)$$

where, X - weight % carbon in the melt

2.1.4 Effect of alloying elements on activity of sulphur

Sherman and Chipman [1] studied activity of sulphur in the iron melt containing various elements like manganese, copper and silicon etc at $1600^\circ C$. They plotted $\log f_s$ vs $[wt\%i]$ (where i may be any alloying element) curve. From the curve e_i^S , can be calculated in each

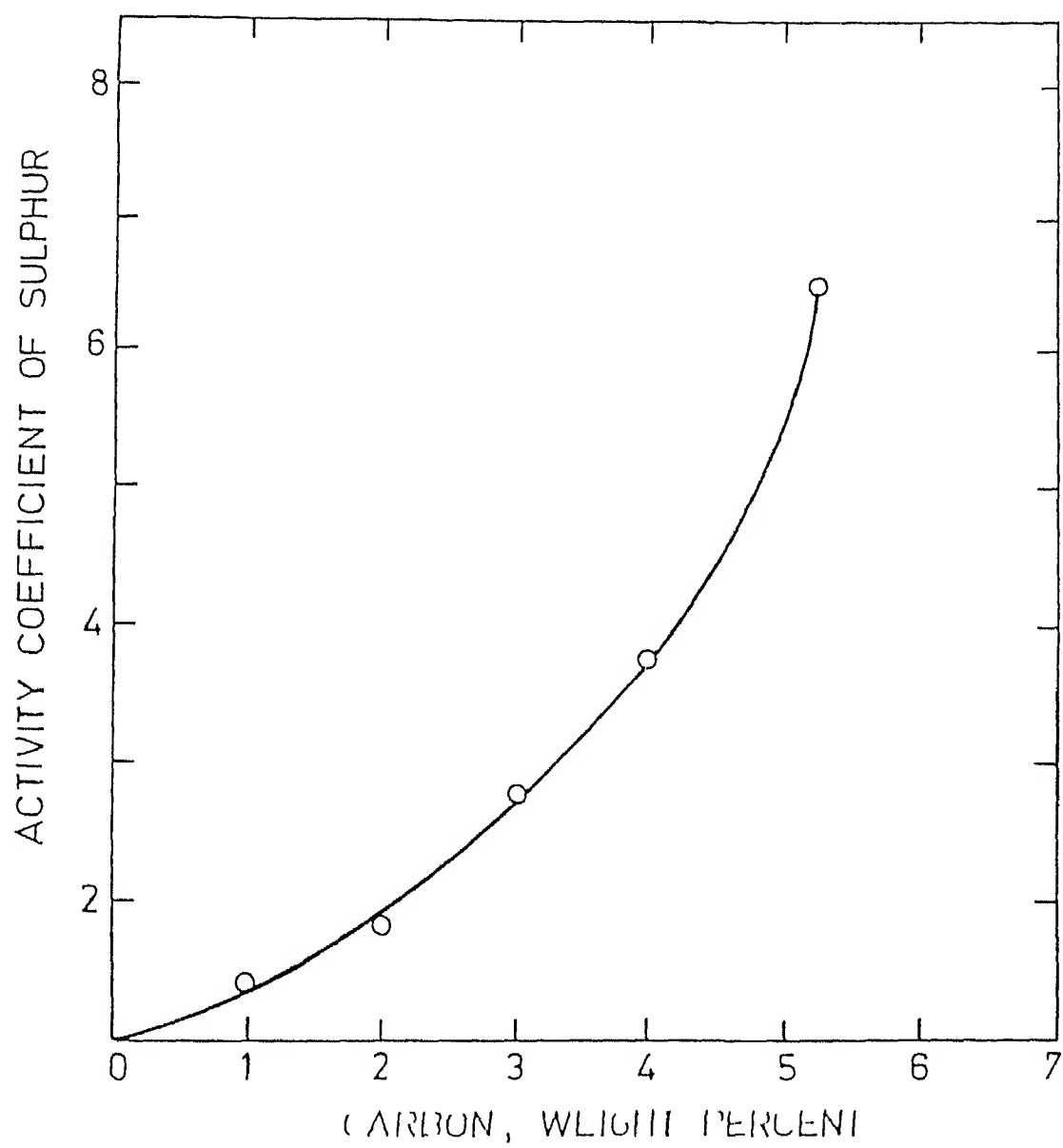


Figure 2 2 Effect of carbon content on activity coefficient of sulphur in iron at 1600°C

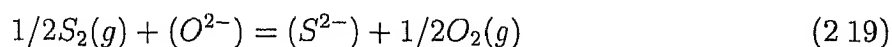
case using equation (2.7). Their results are summarised in Table (2.1) and figure (2.3)

Table 2.1 Summary of interaction parameters obtained by Sherman and Chipman

i	$e_s^i = \frac{\partial \log f_s}{\partial \text{wt}\%i}$
C	+0.113
Si	0.065
P	0.043
Al	0.054
Cu	-0.013
Mn	0.025

2.1.5 Sulphide capacity of the slag

The principal equilibrium reaction between gas and slag may be represented by the following

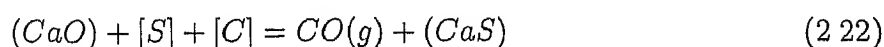


$$K = \sqrt{P_{O_2}/P_{S_2}} (a_S^{--}/a_O^{--}) \quad (2.20)$$

Richardson (4) assumed the henrian behavior of sulphur in slag because of its low solubility in slag and defined a term known as sulphide capacity as follows

$$C_s = \text{sulphide capacity} = (\text{wt}\%S) \sqrt{P_{O_2}/P_{S_2}} \quad (2.21)$$

Venkatrati and Bell (5) tried to express sulphur partition between slag and metal in the blast furnace melt in term of sulphide capacity of slag. Sulphur distribution between slag and metal can be written as



$$\log k = -5960/T + 6.022 \quad (2.23)$$

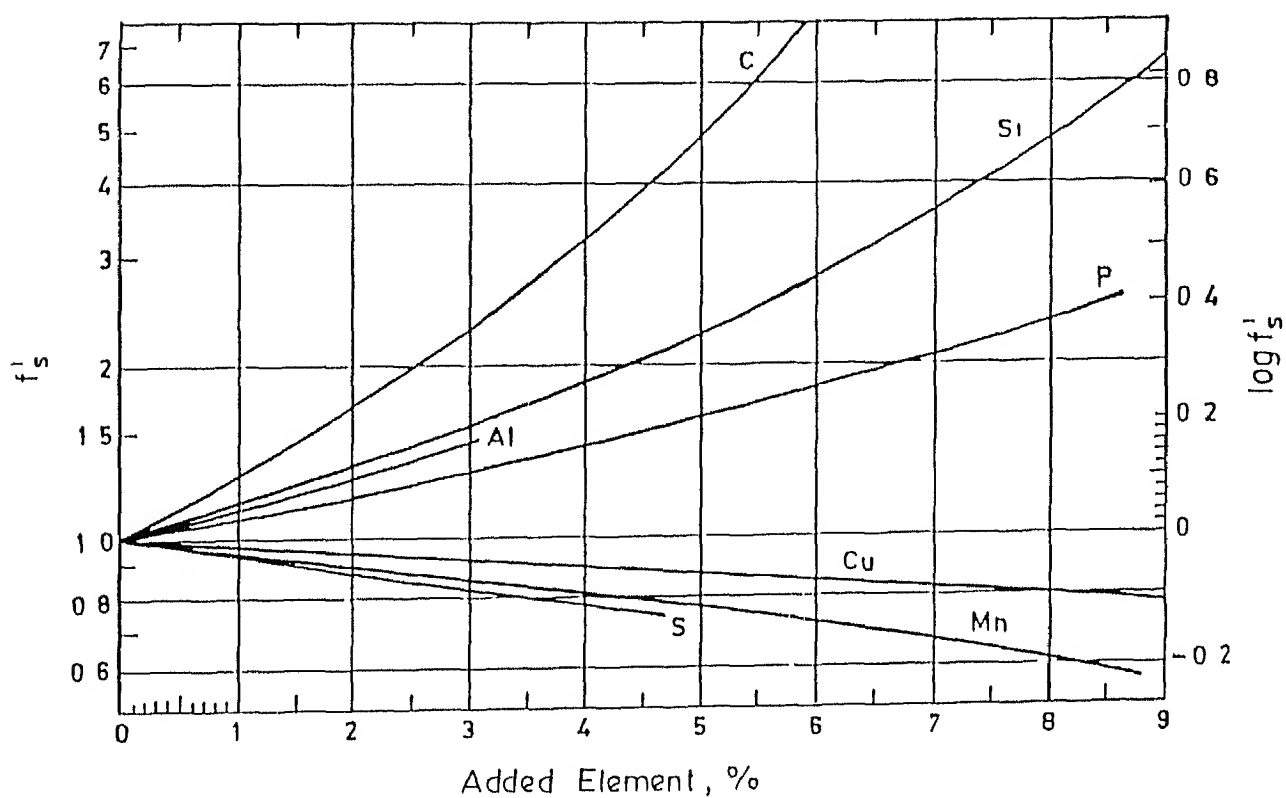


Figure 2.3 Effect of alloying elements on activity coefficient of sulphur in iron at 1600°C

They used the data of Kalyaniam (6) for sulphide capacities in different systems and correlated these data with empirically with ratio $\frac{(N_{CaO}+1/2N_{MgO})}{(N_{SiO_2}+1/3N_{Al_2O_3})}$ where N denotes mole fraction. The plot between $\log C_S$ and $\frac{(N_{CaO}+1/2N_{MgO})}{(N_{SiO_2}+1/3N_{Al_2O_3})}$ at 1500°C is shown in Fig. 2.4

Using the thermodynamic data for sulphur solution and carbon monoxide formation, they proposed a relation between sulphide capacity and sulphur partition ratio as follows

$$\log(\%S)/[a_S] = (5.55 - 7.24/T) + \log C_S + \log(a_C/P_{CO}) \quad (2.24)$$

a_C and a_S are the activity of the carbon and the sulphur respectively. Iron oxide content of slag is a better measure of oxygen potential than the carbon monoxide pressure. Modifying the above equation, they obtained the following

$$\log(\%S)/[a_S] = (5543/T - 1.43) + \log C_S + \log(a_{Fe}/a_{FeO}) \quad (2.25)$$

Kim Kaisud (7) studied the effect of alkali oxide on the sulphide capacity of the slag. The oxides of potassium and sodium in the slag are of interest as alkali are well known to cause problems in the blast furnace iron making in blast furnace (8,9). They gave a relation where effect of MgO and alkali are put together

$$\log C_S = \log C_S^o - 0.01 * [Wt\%MgO - (wt\%MgO^o)] + 0.1 * [wt\%A - (Wt\%A^o)] \quad (2.26)$$

where $wt\%A = 3 \text{ wt}\% K_2O + \text{wt}\% Na_2O$

Subscript o stand for a reference value. C_S^o refers to sulphur capacity in a reference state and $\log C_S^o$ was reported as -3.82 under the following conditions

Temperature 1500°C, basicity $B = 1.2$, 10wt% MgO, 12wt% Al_2O_3

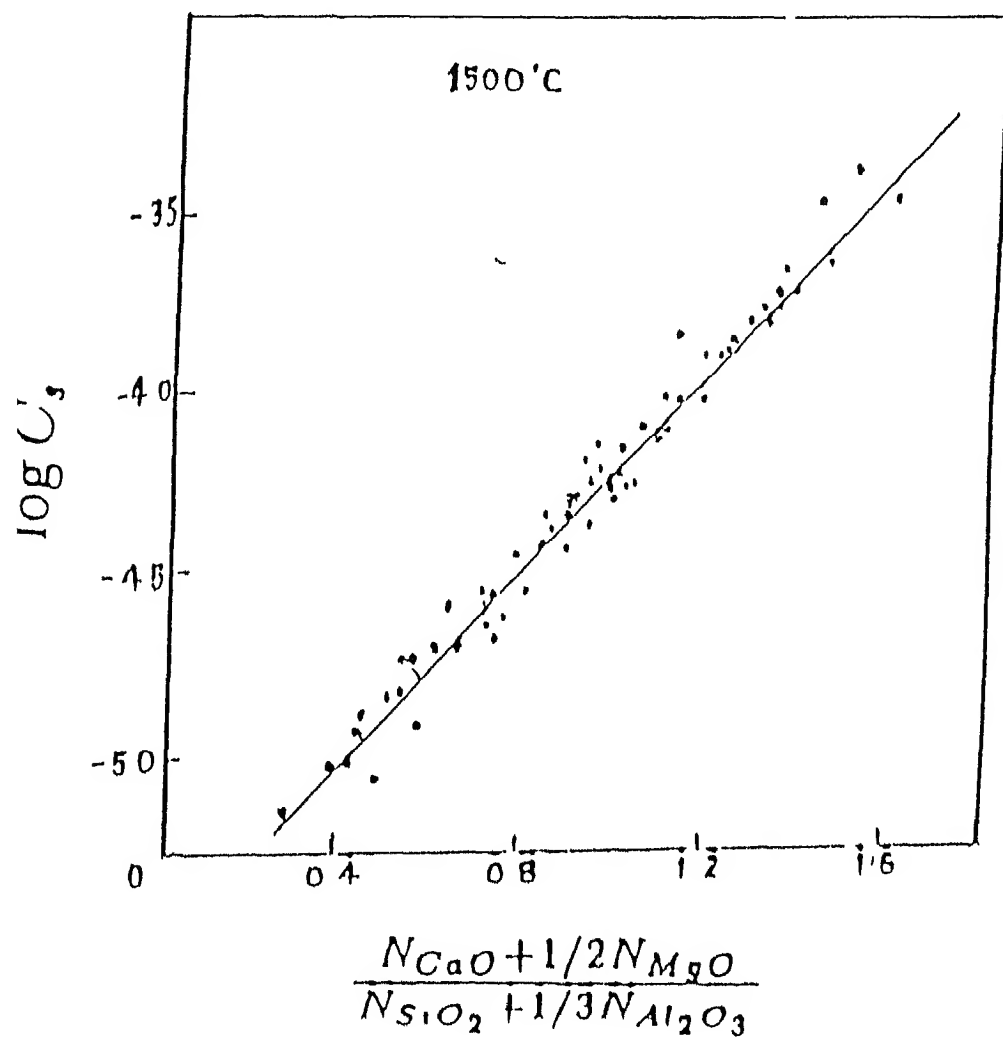
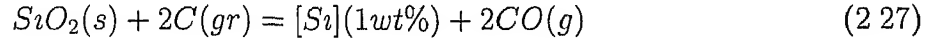


Figure 2.4 Correlation of sulphide capacity measurements with the empirical ratio

2.2 Sulphur distribution between metal and slag in blast furnace

Turkdogan (23) reviewed the reactions occurring in the blast furnace

The equilibrium reaction for distribution of silicon between metal and slag is given as



$$K_{Si} = \frac{[pctSi]\gamma'_{Si}p_{CO}^2}{a_{SiO_2}a_C^2} \quad (2.28)$$

where γ'_{Si} is the activity coefficient of silicon whose value approaches to 15 for carbon saturated melt

In most of the blast furnace slags, the total number of moles of constituent oxides per 100 g of slag is about 1.65. Therefore, the activity of silica, SiO_2 , can be represented in term of weight percent of SiO_2 and its activity coefficient, γ_{SiO_2}

$$a_{SiO_2} = \frac{(\%SiO_2)\gamma_{SiO_2}}{60 + 1.65} \quad (2.29)$$

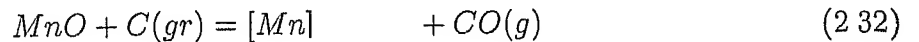
Combining (2.28) and (2.29) and assuming $a_C = 1$ and $[Si] < 2pct$

$$\frac{[\%Si]p_{SiO_2}^2}{(\%SiO_2)} = 7.73 \times 10^{-4} K_{Si}\gamma_{SiO_2} \quad (2.30)$$

the value of γ_{SiO_2} for $CaO - Al_2O_3 - SiO_2$ melt at $1500^\circ C$ may be obtained from work of Rem and Chipman (24). The temperature dependence of K_{Si} is given as

$$\log K_{Si} = \frac{-30935}{T} + 20.455 \quad (2.31)$$

The equilibrium constant for reduction of MnO is evaluated as



$$K_{Mn} = \frac{[\%Mn]\gamma'_{Mn}p_{CO}}{a_{Mn}a_C} \quad (2.33)$$

An estimated value of $\gamma'_{Mn} = 0.8$ may be used for graphite saturated melt. In term of γ_{MnO} , and weight percent MnO

$$a_{MnO} = \frac{(\%MnO)\gamma_{MnO}}{71 + 1.65} \quad (2.34)$$

Abraham et al. (25) have calculated the activity coefficient of MnO γ_{MnO} in $CaO - Al_2O_3 - SiO_2 - MnO$ slag at $1500^\circ C$ and $1600^\circ C$

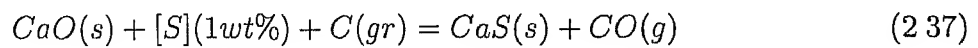
For unit activity of carbon we have

$$\frac{[\%Mn]p_{CO}}{(\%MnO)} = 1.07 \times 10^{-7} K_{Mn} \gamma_{MnO} \quad (2.35)$$

Temperature dependence of equilibrium constant K_{Mn} is given as

$$\log K_{Mn} = \frac{-15090}{T} + 10.970 \quad (2.36)$$

In the blast furnace, the sulphur reaction may be represented by



$$K_S = \frac{a_{CaS}p_{CO}}{a_{CaO}[\%S]\gamma'_S a_C} \quad (2.38)$$

The temperature dependence of the equilibrium constant, K_S , is given by

$$\log K_S = \frac{-6010}{T} + 5.935 \quad (2.39)$$

The activity of CaS and CaO relative to pure solids may be represented in term of weight percent of CaS and CaO and their activity as

$$\frac{a_{CaS}}{a_{CaO}} = \frac{56(\%S)\gamma_{CaS}}{32(\%CaO)\gamma_{CaO}} \quad (2.40)$$

In a graphite saturated melt, the activity coefficient of sulphur, γ'_S , is around 7.

Inserting this in equation (2.38) and combining this with (2.40) we have

$$\frac{(\%S)p_{CO}}{[\%S]} = 4 \frac{\gamma_{CaO}(\%CaO)K_S}{\gamma_{CaS}} \quad (2.41)$$

Ratio of $\frac{\gamma_{CaO}}{\gamma_{CaS}}$ is derived from data of Abraham(26)

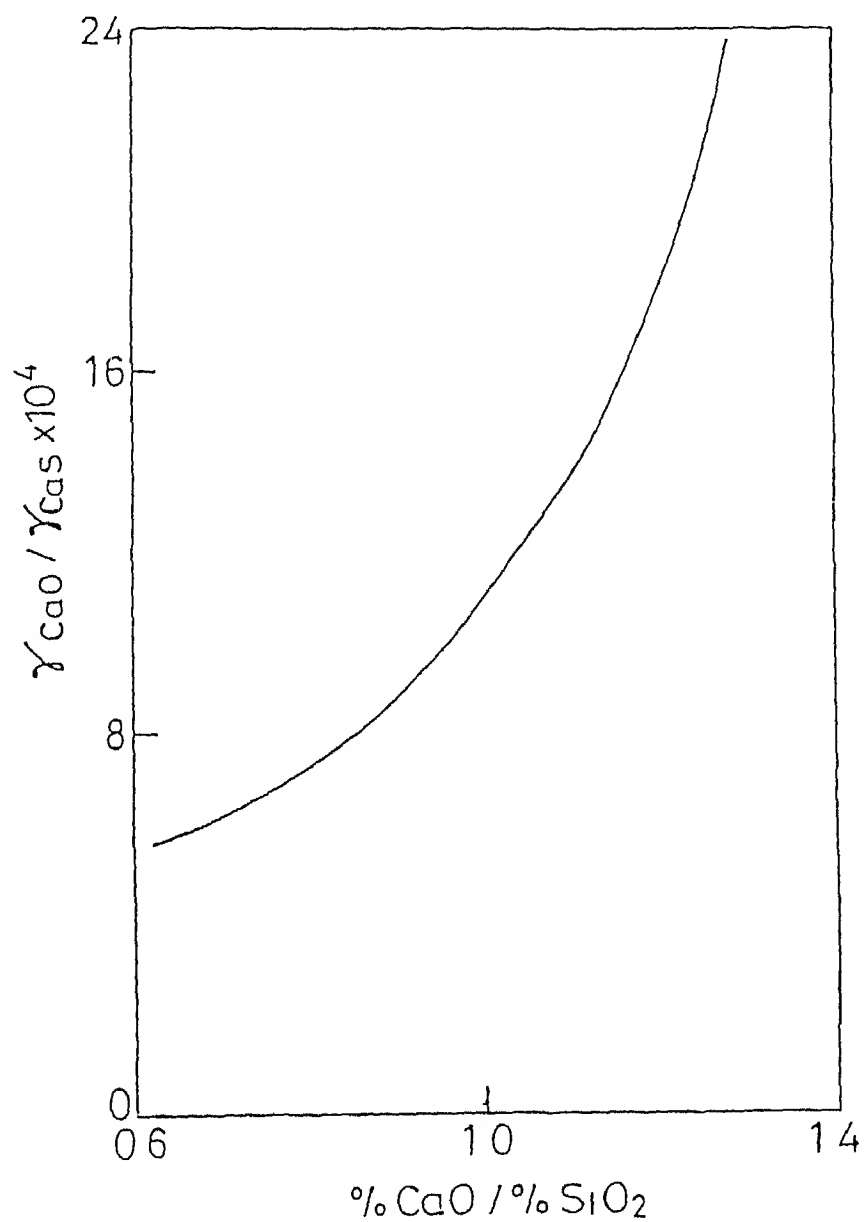
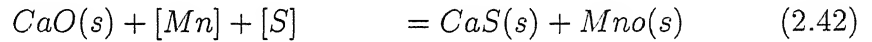


Figure 2.5 Lime / Sulphide activity coefficient ratio at $1500^{\circ}C$ in calcium silicate melt saturated with CaS

Turkdogan (26) as well as Biswas (27) has shown that the primary reactions for the transfer of manganese, silicon and sulphur from metal to slag do not reach equilibrium in blast furnace due to three phases involved in these reactions. However, coupled reactions more or less reach equilibrium in the blast furnace. Some important coupled reactions are described in the following section.

1 Reaction involving manganese and sulphur is:

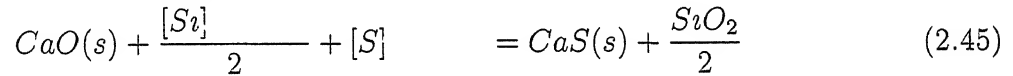


$$K_{MS} = \frac{K_S}{K_{Mn}} = \frac{a_{CaS}a_{MnO}}{a_{CaO}[\%S][\%Mn]\gamma'_{Mn}\gamma'_S} \quad (2.43)$$

Combining this with equation (2.33), (2.39) and (2.40) gives

$$\frac{(\%S)}{[\%S]} = 374 \left(\frac{K_S \gamma_{CaO} \%CaO}{K_{Mn} \gamma_{CaS} \gamma_{MnO}} \right) \frac{[\%Mn]}{(\%MnO)} \quad (2.44)$$

2 Reaction involving silicon is given as



$$\frac{(\%S)}{[\%S]} = 154 \frac{K_S \gamma_{CaO} \%CaO}{\sqrt{K_{Si} \gamma_{CaS} \sqrt{\gamma_{SiO_2}}}} \frac{\sqrt{[\%Si]}}{\sqrt{(\%SiO_2)}} \quad (2.46)$$

The graph between $\frac{(\%S)}{[\%S]}$ vs. $\frac{[\%Mn](CaO)}{(\%MnO)}$ is given in Fig (2.6). With the given data, sulphur-manganese equilibrium at graphite saturation is represented as

$$\log \frac{(\%S)(\%MnO)}{[\%S][\%Mn]} = 9080/T - 5.832 + \log(\%CaO) \quad (2.47)$$

For sulphur-silicon reaction, the equilibrium relation may be given as

$$\log \frac{(\%S)\sqrt{\%SiO_2}}{[\%S]\sqrt{[\%Si]}} = 9080/T - 5.832 + \log(\%CaO) + 1.396B \quad (2.48)$$

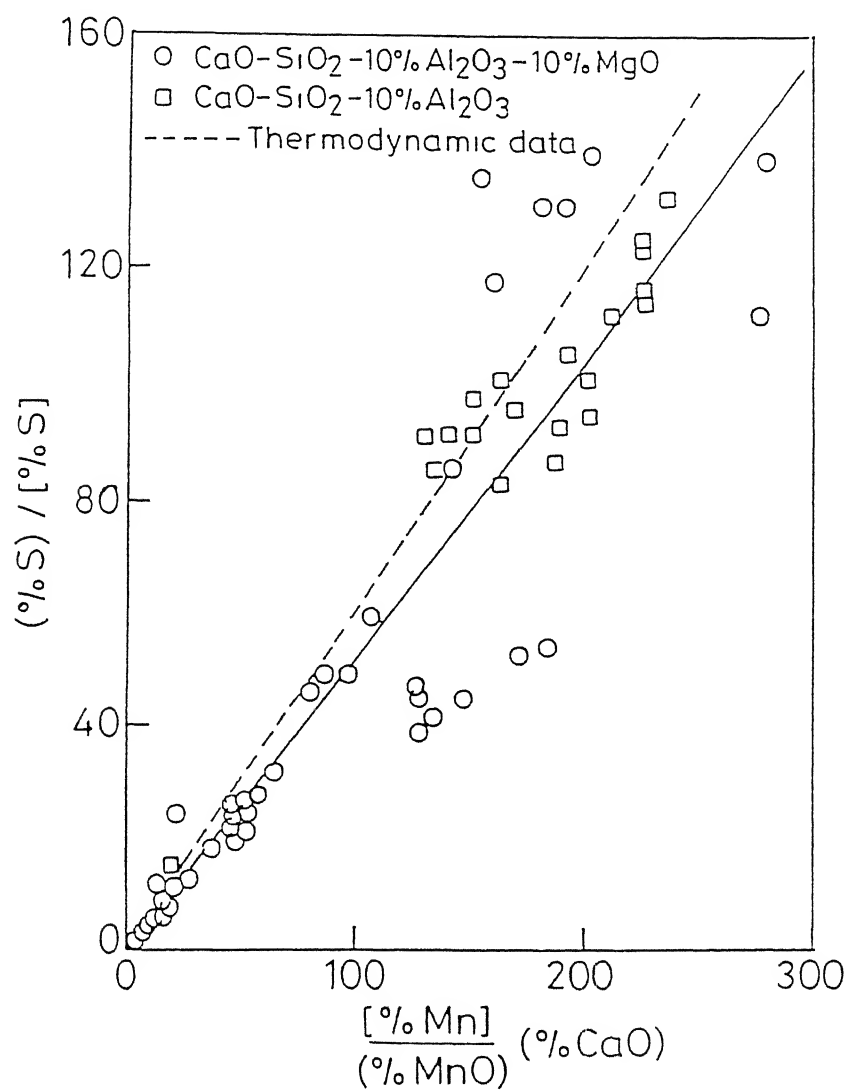


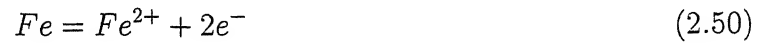
Figure 2.6: Sulphur – manganese reaction equilibrium at graphite saturation and $1500^{\circ}C$

2.3 Mechanism and Kinetics of Desulphurization

King and Ramachandran (10) have demonstrated that the transfer of sulphur to carbon saturated-non-slag system is electrochemical in nature. When the sulphur is transferred from metal to slag, electrons must be provided as given below.



Since the electroneutrality is maintained in the slag and the metal in the absence of an electric field across the slag metal interface, the solute in the metal becomes oxidised to provide electron needed for the necessary requirement as follows.



Therefore, in presence of these solutes in iron, the transfer of n_S moles of sulphur from metal to slag is always accompanied by the transfer of an equivalent moles of solutes to satisfy the stoichiometric requirement. The balance is given as

$$2n_S = 2n_{Fe} + 2n_{Mn} + 3n_{Al} + 4n_{Si} + 2n_c \quad (2.56)$$

J C. Fulton (11) have studied the effect of stirring on the desulphurization rate. To analyse their data, they assumed that transfer of sulphur from bulk metal to phase boundary controlled the rate of overall reaction and they obtained following expression

for transfer of sulphur from metal to slag phase .

$$\frac{V dC'_S}{dt} = - \frac{D'_S A (C'_S - C_S^*)}{\delta'_S} \quad (2.57)$$

$$2.3 \frac{d \log(C'_S - C_S^*)}{dt} = - \frac{D'_S * A}{\delta'_S V} \quad (2.58)$$

where C'_S = concentration of sulphur in the bulk metal at any time in *moles/cm³*

C_S^* = equilibrium concentration of sulphur in the metal.

D'_S = diffusion coefficient of sulphur in the metal.

δ'_S = effective boundary layer thickness for sulphur in the metal.

A = area of the slag metal interface.

V = volume of metal.

t = time

For simple geometry $V/A = L$ and expressing concentration in *Wt%*, δ'_S can be calculated from the slope of $\log([\%S] - [\%S^*])$ vs time as follows.

$$\delta'_S = \frac{D'_S}{2.3 * L * slope} \quad (2.59)$$

Then, results are plotted in Fig (2.7) from which it is clear that stirring rate effects the kinetics of reaction. They found that in the early stages of each experiment, curve is non-linear. This is attributed to increase in slag-metal interfacial area.

In a review paper on equilibrium and kinetics of slag metal reaction, Yasuji (12) examined effects of various factors on the rate of desulphurization. Fig. (2.9) shows the effect of slag composition on the rate of desulphurization. The rate can be expressed as the first order reaction. It was found that the rate increased with an increase in the basicity of slag. Mathematically one may obtain the following.

$$\frac{W_S}{100A} \frac{d\%S}{dt} = K_m[\%S] - K_S[\%S] \quad (2.60)$$

K_m and K_S are the mass transfer coefficient for sulphur in the metal and slag phase respec-

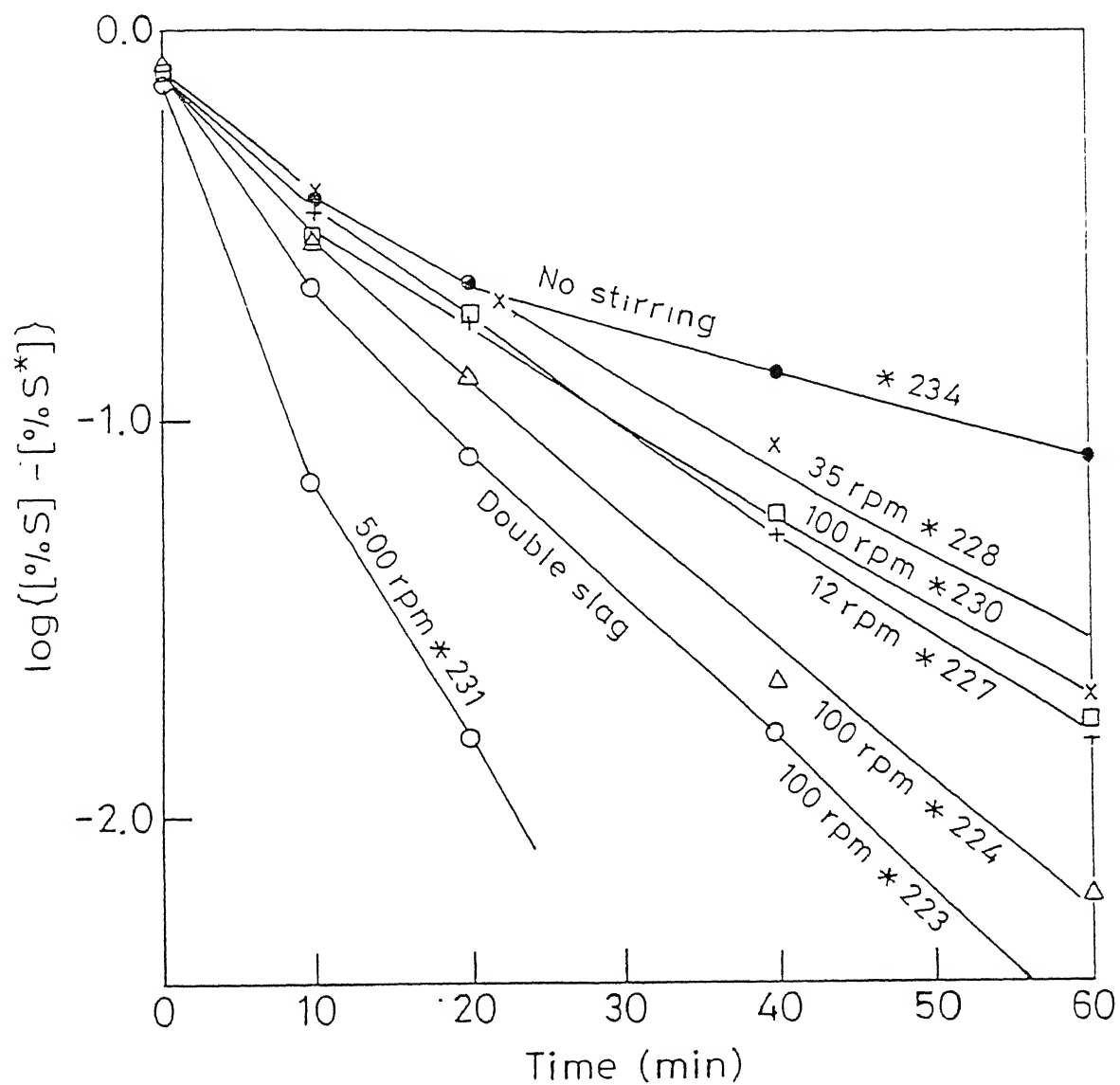


Figure 2.7. Effect of stirring on the desulphurization rate

CENTRAL LIBRARY
I. I. T., KANPUR
No. A 126864

tively Values of K_m and K_s as obtained by them are plotted against slag basicity in Fig. 2.8

K_m increases with increasing slag basicity, but K_s decreases. The fact that rate depends on slag composition suggests that desulphurization process depends upon the diffusion of sulphur in the slag. Desulphurization rate can be expressed as follows.

$$\frac{d\%S}{dt} = -\frac{A * D_S * \rho_s}{V_m * \delta_s * \rho_m} * ([\%S]^i - [\%S]) \quad (2.61)$$

Where ρ_s and ρ_m are densities of iron and slag, D_S is the diffusivity of sulphur in the slag, δ_s is the thickness of boundary layer of slag.

Froberg (13) studied the kinetics of sulphur transfer from metal containing different amount of C, S, Mn, Al, Si and Ti to lime silica slag at 1600°C. They found that the presence of Al, Ti, Mn and Si in metal increases the rate of desulphurization. They also found reversion of Fe, Mn, Ti from slag to metal phase. To explain their observations, a mechanism of sulphur transport was proposed. It consists of the following three steps:

- 1) Transfer of sulphur and other reactants from the bulk to slag metal interface.
- 2) Reaction at the interface.
- 3) Transport of products away from interface.

It was assumed that interfacial reaction controlled the rate of transfer of sulphur as the activation energy for interfacial reactions was much higher than that for transport phenomena. They proposed that desulphurization process could be expressed through the following rate equation.

$$J_s^t = 1/2 \sum_{i=1}^N Z_i [K_i a_i^M \exp(\frac{Z_i(\mu_S^{M'} - \mu_S^{S'})}{Z_S RT}) - K_i a_i^S \exp(-\frac{Z_i(\mu_S^{M'} - \mu_S^{S'})}{Z_S RT})] \quad (2.62)$$

where a_i^M and a_i^S = activity of element i in metal and slag phase respectively.

J_i^t = Transport rate of component i

K_i = specific reaction rate of element i

Z_i = charge on element i

R = gas constant

T = absolute temperature

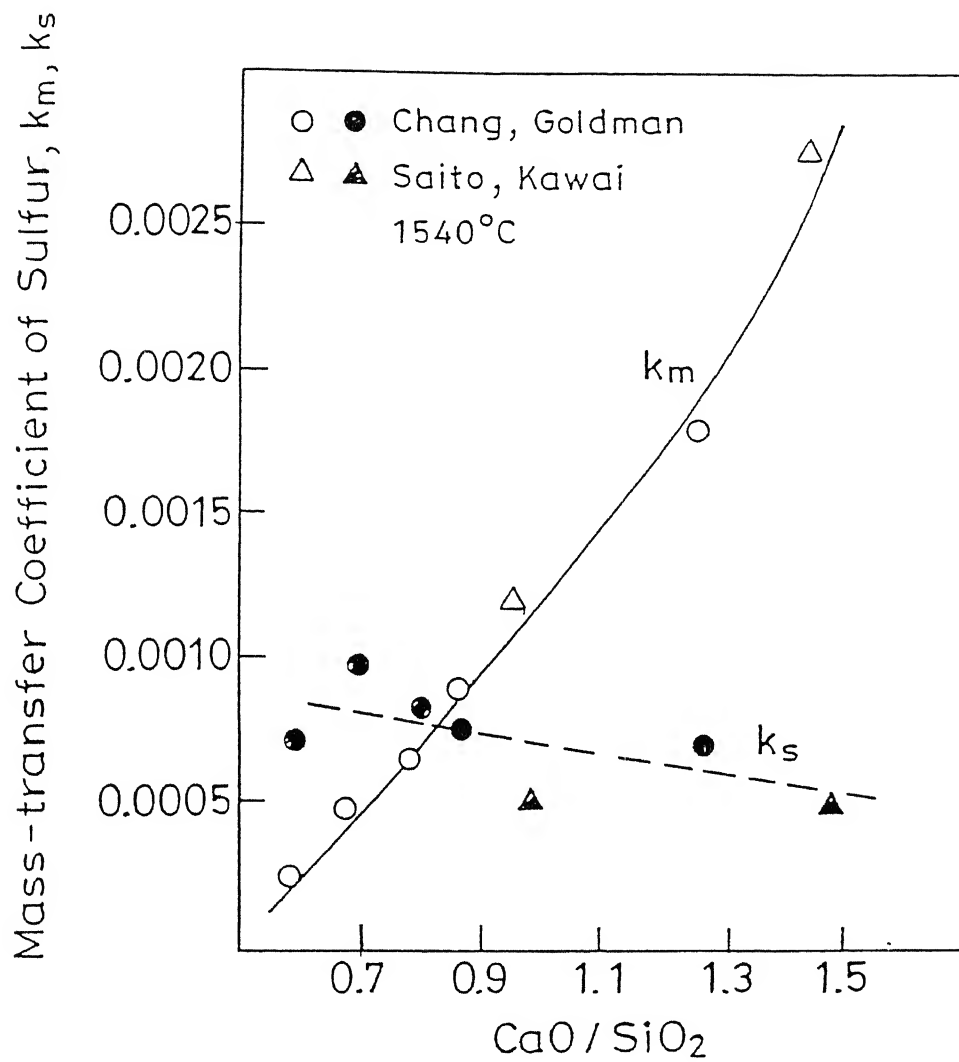


Figure 2.8. Relation between mass transfer coefficient, K_m and K_s , and basicity of slag

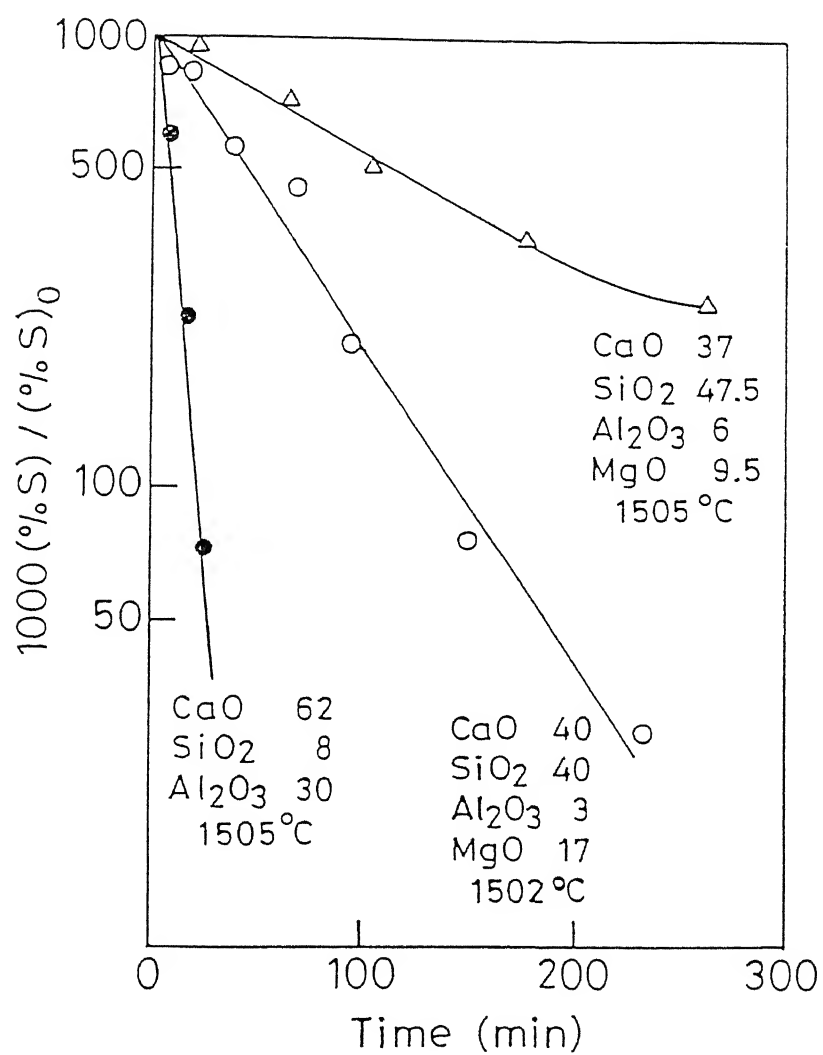


Figure 2 9. Concentration change of sulphur in liquid iron in slag of different basicities

$\mu_S^{M'}$ and $\mu_S^{S'}$ = Chemical potential of the sulphur at the interface in metal and slag phases respectively

2.4 External Desulphurization of Hot metal

Due to importance of external desulphurization of hot metal, many studies on the kinetics of desulphurization by injection of calcium carbide, magnesium, lime and calcium alloys etc in the blast furnace iron have been reported in the literature. These studies are helpful in enhancing our knowledge of desulphurization process from industrial point of view. Most of these studies are done on pilot plant scale. The various methods of pretreatment of metal are summarised in Table 2.2.

Table 2.2: Method of desulphurization

Desulphurizing agent	Mode of addition	Reagent quantity kg / THM	Sulphur range
Soda ash	bulk addition	10	0.10 to 0.035
Lime	injection	10 to 20	0.05 to 0.02
lime and soda ash	injection	8 to 10	0.05 to 0.02
Calcium carbide	injection	4	0.05 to 0.02
Magnesium coke	plunging	0.7	0.048 to 0.022
Magnesium granules	plunging	0.7 to 1.2	0.05 to 0.005

Lime is capable of reducing sulphur content of cast iron and blast furnace iron to very low level but the rate of desulphurization is low. It may be attributed to solid reaction products that form a diffusion barrier on the surface of lime particles.

Craig F Landefeld (14) have studied effect of lime and spar addition in the melt. Results are plotted in Fig (2.10). Addition of spar increases the rate of desulphurization. However, under the experimental conditions, the rate of desulphurization was found to remain un-

changed beyond 8% spar. This is attributed to saturation of liquid phase with $3CaO.SiO_2$ phase. They also compared the effects of Si and Mn on desulphurization rate. Results are plotted in Fig (2.11). Magnesium is used to desulphurize the metal from blast furnace iron. However, injection of magnesium into blast furnace iron has been a major problem. Boiling point of magnesium is $1107^\circ C$ and it tends to explode when plunged into hot metal whose temperature commonly exceeds $1200^\circ C$. Iron et al. (15) have circumvented the problem by vapourizing the magnesium before it was injected into iron and studied the kinetics of desulphurization, based on MgS precipitation.

External desulphurization of hot metal by calcium carbide injection in the melt is a well established process. Chang (16) have studied the kinetics of desulphurization of hot metal at temperature of $1350^\circ C$ and reported that the oxygen activity of the bath is very important factor during desulphurization. Control of hot metal oxygen activity to low levels improved the efficiency of desulphurization process. They found that there was an incubation period during which reagent created an appropriate slag layer before it began to remove the sulphur.

With no slag, the melt surface was susceptible to oxidation and a liquid layer of iron oxide was probably formed. This slag could then oxidize the calcium sulphide produced during the desulphurization process thus reverting the sulphur into iron melt. The net effect was that no desulphurization occurred in the incubation period. As the partially oxidized CaC_2 / CaS particles continued to build up on the surface during injection, conditions would become more and more reducing, thereby favouring desulphurization. In case of unreactive slag mixture of $CaO - SiO_2$, an oxide rich slag could be formed, which must be reduced before effective desulphurization could proceed.

Tabala (17) proposed a reaction mechanism according to which calcium carbide first decomposed to form graphite and calcium vapours. The calcium vapours then reacted with sulphur to form a layer of calcium sulphide over the graphite layer. The layers of graphite and calcium sulphide progressively thicken so that calcium vapour must diffuse through them. Chiang et al. (18) showed that the rate of calcium diffusion through the product layer was 50

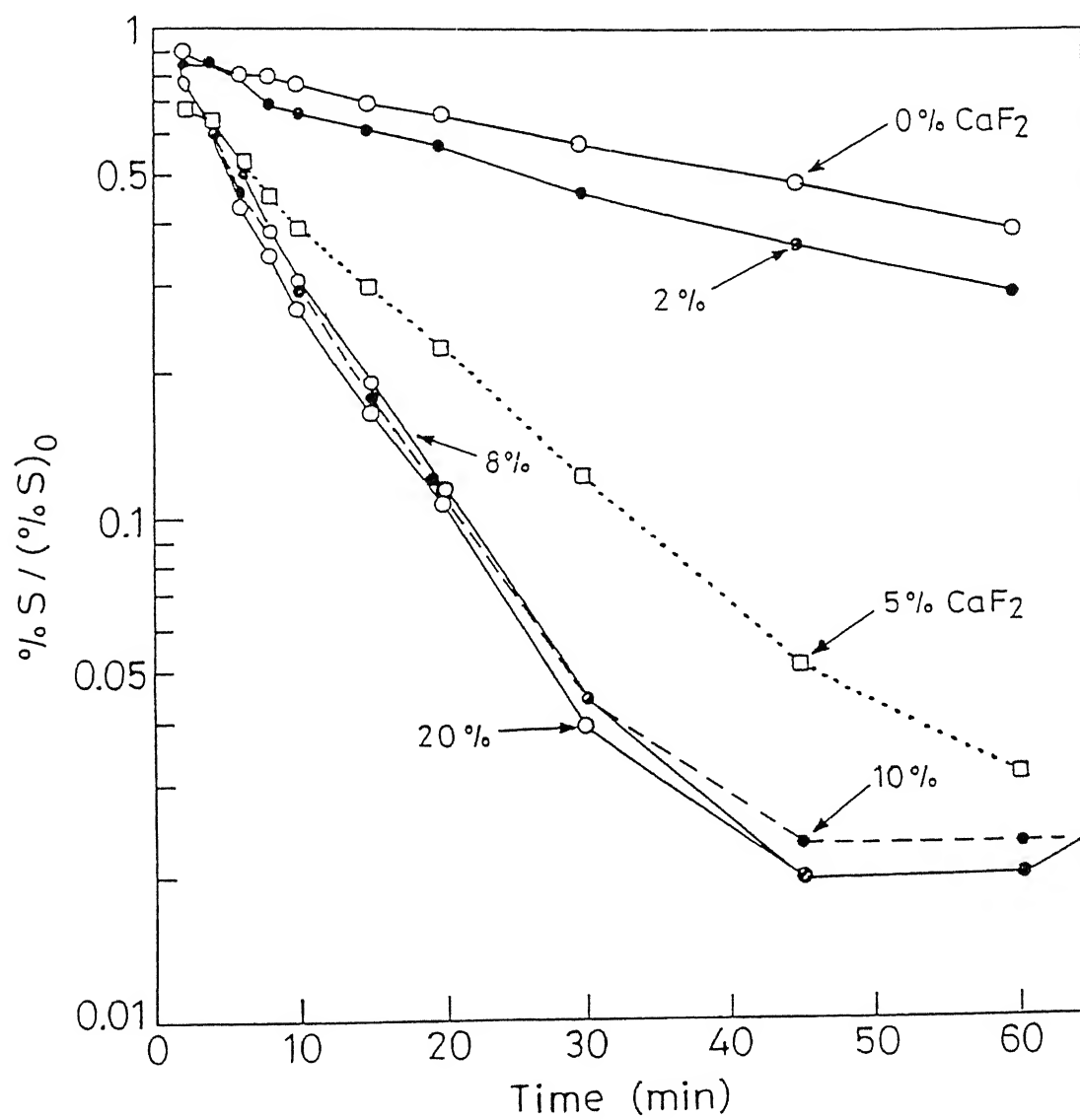


Figure 2 10 Effect of CaF_2 percentage on desulphurization

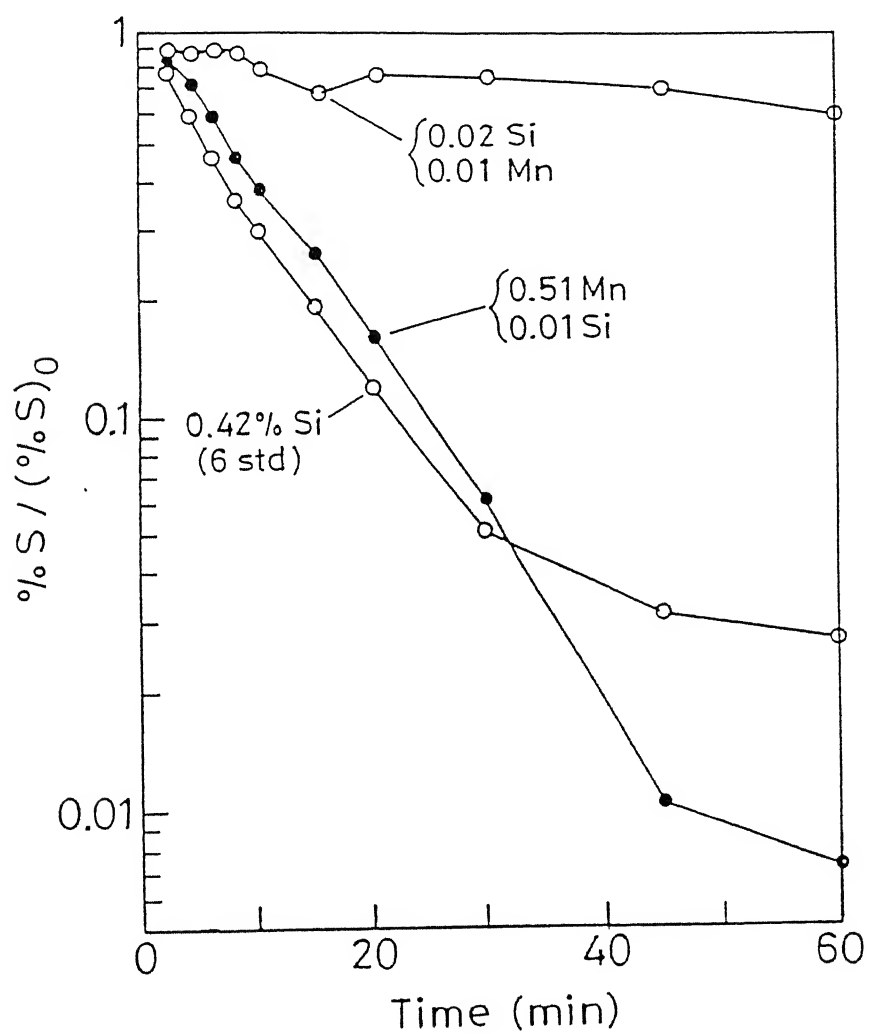


Figure 2.11. Comparison of the effects of Si and Mn

times greater than the rate of sulphur diffusion through the particle/liquid boundary layer. Based on these facts, they concluded that desulphurization rate was determined by the rate at which sulphur diffused through the liquid boundary layer around the particles rather than the product layer.

External desulphurization process has some limitation which may be due to inherent difficulties encountered during external desulphurization process. Some of the problems that are encountered are^{as} below:

- (1) Freezing of top layer of metal in the ladle may occur to give high skull losses. This makes addition of desulphurizing agent to bath very difficult.
- 2) Sulphur rich blast furnace slag may accompany the metal. In some cases it may lead to increase in the sulphur in sulphur load.
- 3) Ladle lining may get damaged due to addition of desulphurizing agents.
- 4) limitation on effectiveness of desulphurizing agents makes the process plant specific.

2.5 Effect of Manganese on desulphurization

Oelsen (19) studied the solubility of MnS in carbon saturated blast furnace iron and reported that the solubility of MnS decreased with decreasing temperature. Results are plotted in Fig (2.11). Si and P content of the blast furnace iron was not specified by Oelsen. Morris (20) studied Mn-S equilibrium in Fe-C alloys by step wise addition of manganese. His results are plotted in Fig (2.12).

Morris concluded from his data that manganese alone could not be an efficient desulphurizer except at temperature below the normal operating range. However, he predicted that in presence of an oxide slag, manganese could be a more effective desulphurizer due to lower activity of manganese sulphide in the slag. Grant (21) studied the effect of Mn and MnO when added to initial charge or during the course of a heat. Addition of MnO led to an immediate and temporary reversion of sulphur to the melt. This was ascribed to the increase in oxygen potential of slag. Effect of Manganese on desulphurization rate was very small and it

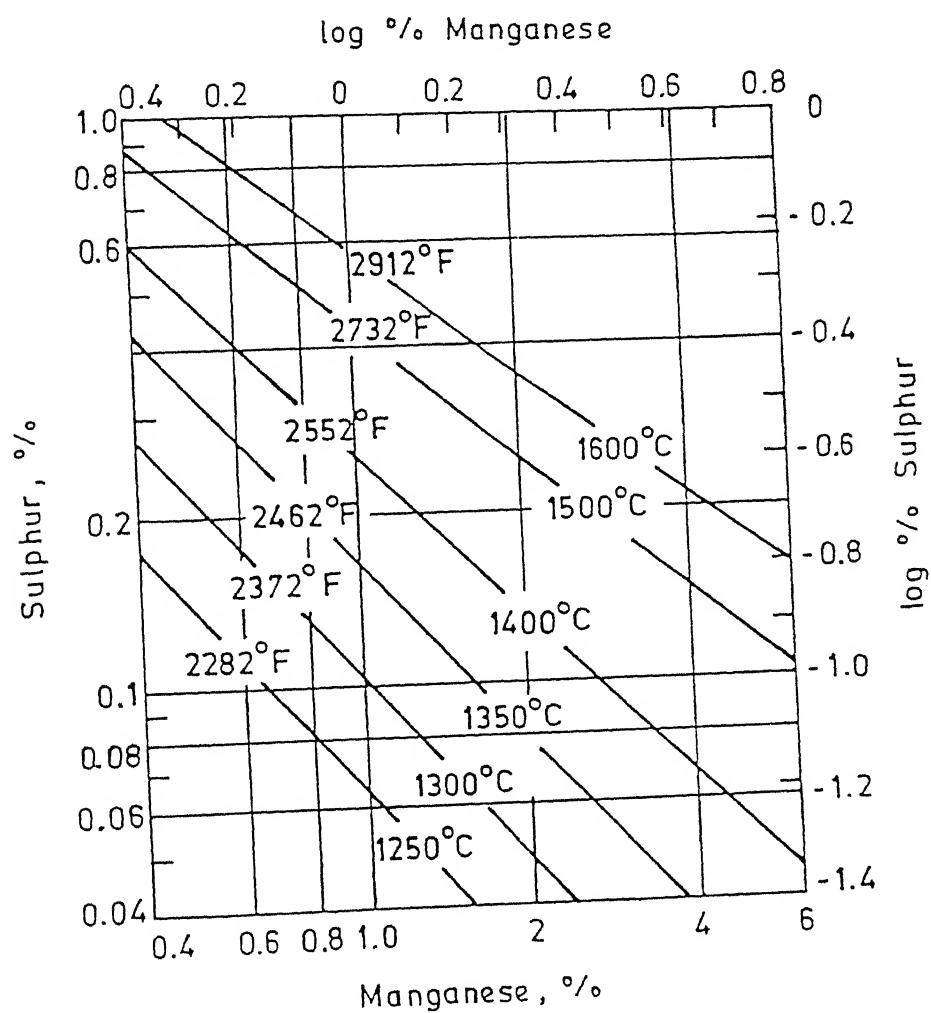


Figure 2.12· manganese sulphide solubility in the Iron-carbon melt

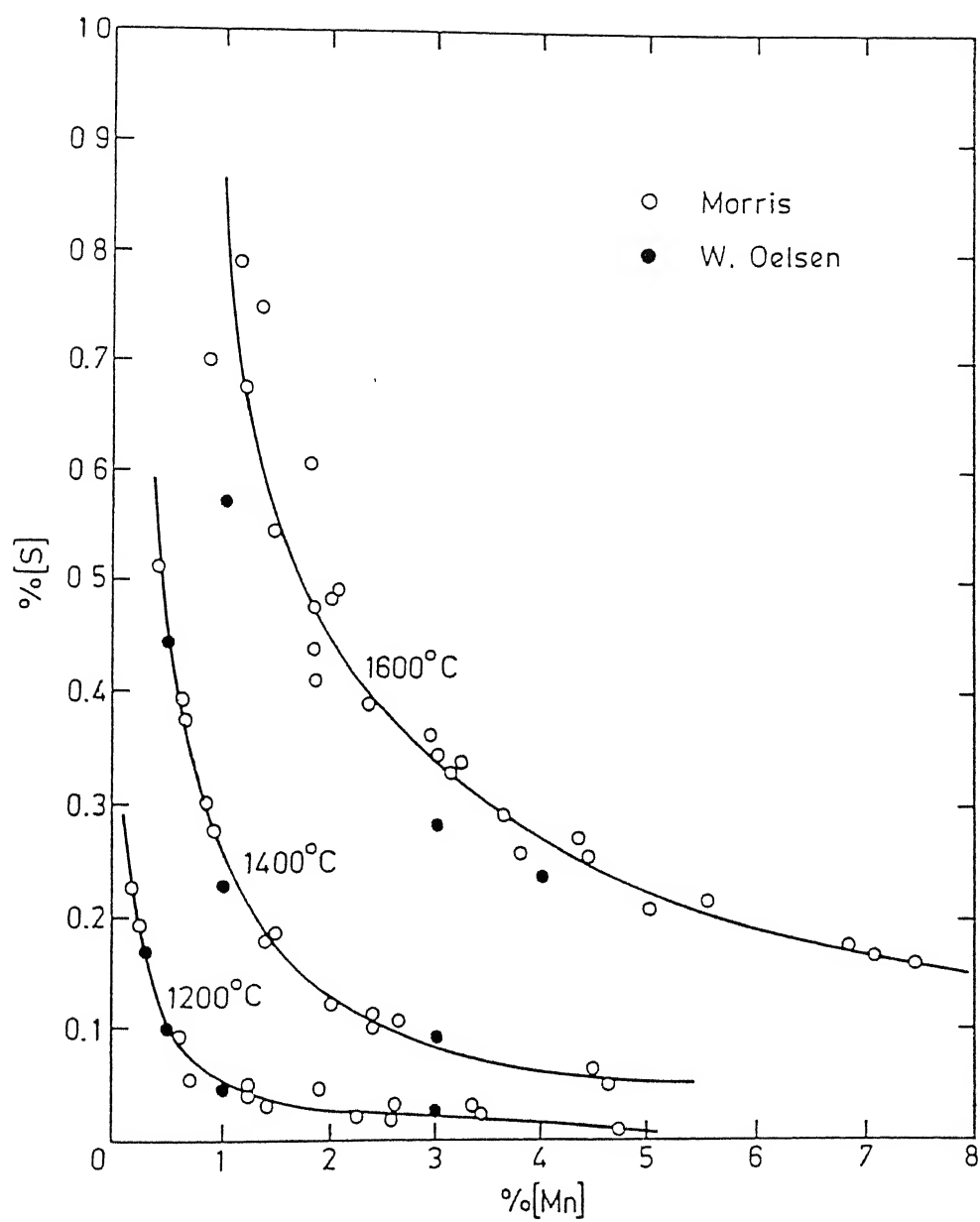
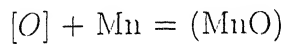
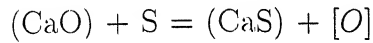


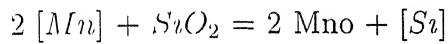
Figure 2.13: Effect of manganese on the sulphur content of the carbon saturated melts of iron in equilibrium

was confined to less basics slags. Pattjoshi (22) showed that with an increase in manganese level in the melt, there was increase in transfer of sulphur to slag phase. Following reasons were attributed to this;

- 1 The activity of MnS was lowered due to presence of liquid lime based slag.
- 2 Manganese enhanced the rate of sulphur removal by CaO in the slag as per the following reactions



(3) Manganese in the melt reacted with SiO_2 in the slag to form silicon in the melt and MnO as per the reaction



This would increase the basicity of the slag which lowers sulphur in the melt.

He suggested that all the three factors listed above might be responsible for lowering of sulphur level in presence of manganese in the melt.

Chapter 3

EXPERIMENTAL DETAIL

3.1 Materials

Solid pig iron samples were obtained from Bhilai Steel Plant. They were broken into small pieces so that they could be charged to the graphite crucible. Manganese used was 99% pure in the form of flakes. Iron sulphide, silica and alumina used in the study were of GR grade. Lime used was obtained from Ranbaxy India Limited. 4 mm dia and 500 mm long quartz tubes were used to draw samples. One tube could be used for drawing 3 to 4 samples. Standard steel and cast iron sample supplied by NML, Jamshedpur were used to calibrate the set up to determine manganese and sulphur in samples. 50-60 mm high graphite crucible were machined from 50 mm dia, graphite rod.

3.2 EQUIPMENTS

3.2.1 Super Kanthal Raising Hearth Type Furnace

One raising hearth type furnace i.e., model 70 R 10 manufactured and installed by Bysakh and Company, Calcutta was used for doing a series of experiments in the present study. It has got dimensions of 200 mm square \times 300 mm high. The furnace consists of 3 numbers of U shape Molybdenum Disilicide heating elements of type '33'. The furnace has got Pt - 6% Rd/Pt - 30% Rd thermocouple for temperature measurements and a proportional temperature controller. The furnace required a power supply of 2 phase AC of 400 volt. The furnace bottom has a opening of 120 mm and its refractory end was raised or lowered using a lever arm for closing and opening the furnace bottom respectively.

3.2.2 Silicon Carbide Furnace

One silicon carbide furnace having outer diameter of 600 mm and length 400 mm was fabricated in the laboratory. Schematic of the furnace is shown in Fig 3.1. The furnace tube consisted of an alumina tube of 65 mm i.d. and 600 mm long, with one end closed. It rested on a refractory base at the bottom. The tube was filled with alumina powder up to the level of high temperature zone in the furnace. The power to the furnace was supplied using a 40 A single phase oil cooled auto-transformer with 220 volts input and 0 - 240 volt output. Pt - Pt - 10% Rh thermocouple was used to measure and control the temperature. One on - off temperature controller and magnetic relay switch were used to keep the temperature of the furnace in a narrow range.

3.2.3 Digital Balance

The digital balance supplied by the Mettler, Germany, was used to determine the weight up to the accuracy of 0.1 mg for doing chemical analysis of the samples for sulphur and manganese determination.

3.2.4 Sulphur Analysis Set-up

Schematic of the apparatus used to determine sulphur content of samples is shown in Fig. 3.2. It consists of 500 cc conical flask, B/34 sealing joints, separating funnel, 6 mm dia glass tubing, 100 cc measuring cylinder and 1500 watts hot plate. Titration set up consisted of a 25 cc burette and a 10 cc pipette.

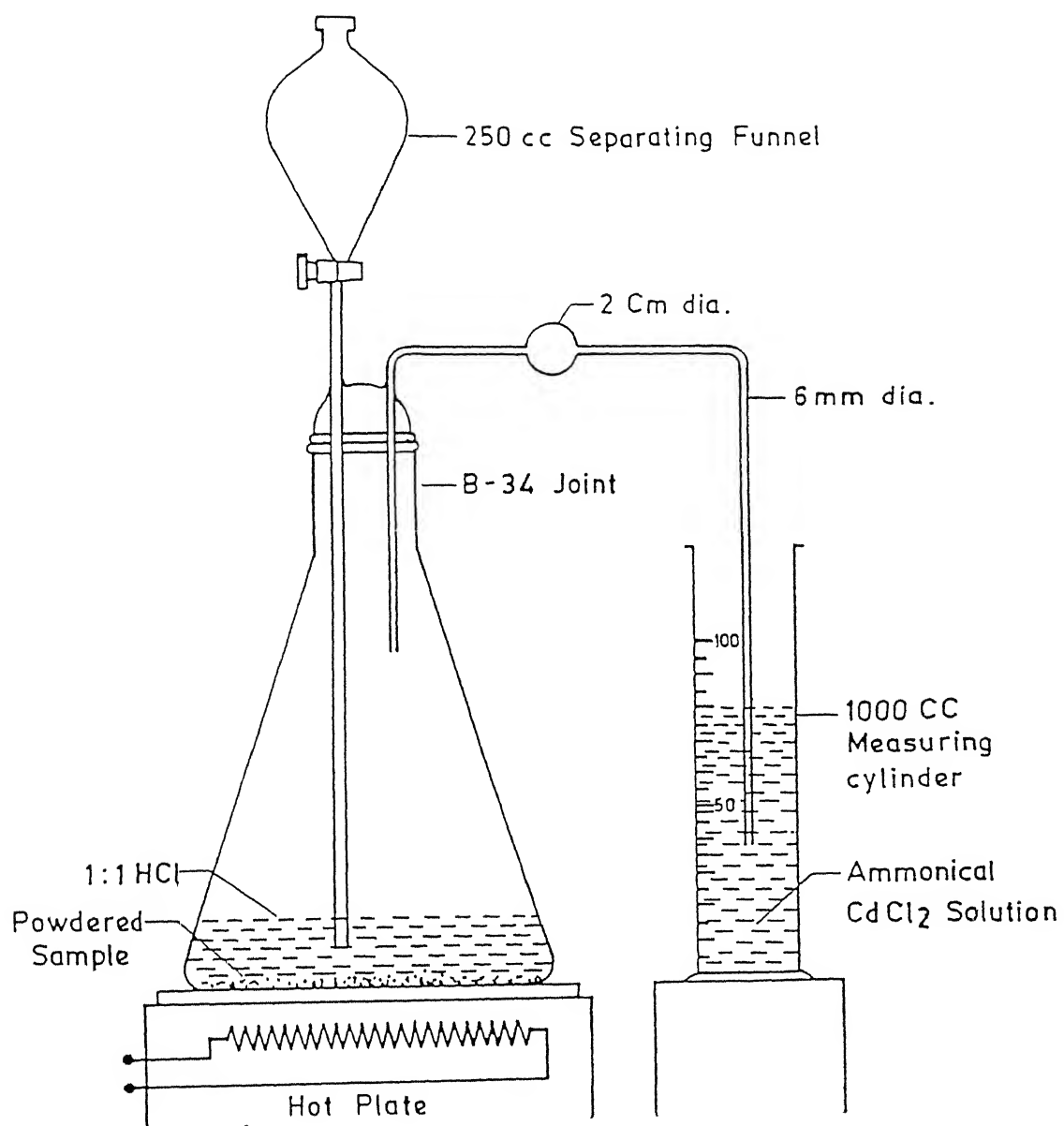


Figure 3 2: Schematic set up for sulphur analysis

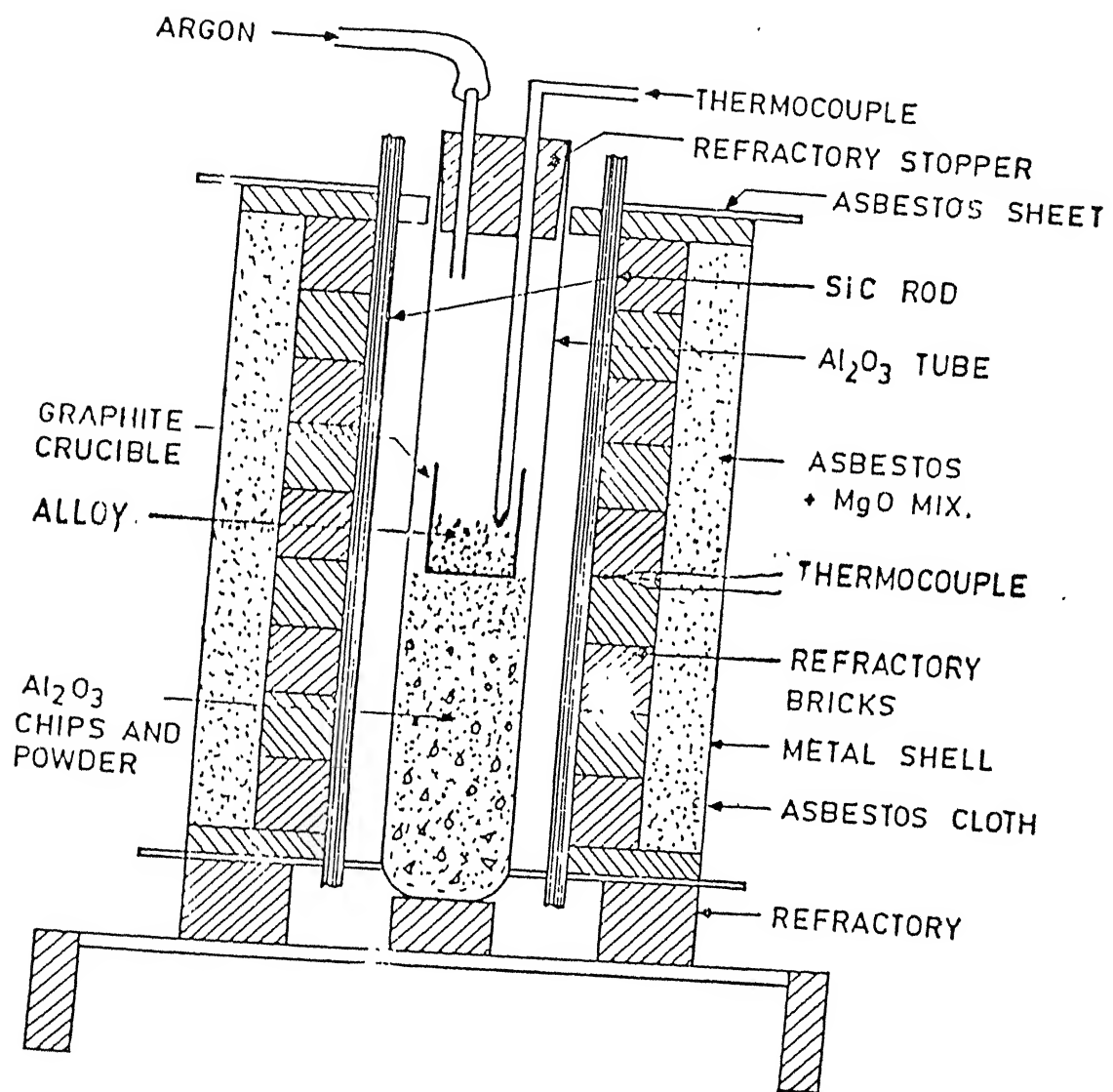


Figure 3.1: Schematic diagram of silicon carbide furnace

3.2.5 Photospectro meter

Manganese analysis was done using Ultra-Violet-Visible Range Spectrophotometer supplied by Systronics, New Delhi

3.2.6 Flow Meter

One capillary flow meter was used to determine flow rate of argon. The flow meter was calibrated using a soap bubble meter.

3.3 Experimental Procedure

3.3.1 Master Slag Preparation

One master slag was made in the laboratory by melting 10 g of alumina, 20 g of lime and 20 g of silica in a graphite crucible. The crucible was heated to 1500°C and held there for 2 h before cooling it to room temperature. The slag was recovered by breaking open the crucible.

3.3.2 Melting of Metal and Slag Phase in Silicon Carbide Furnace

80 to 100 g of blast furnace metal pieces along with required additives such as iron sulphide, manganese metal and slag components were added to a graphite crucible. The crucible was lowered into the hot zone of the silicon carbide furnace using a steel rod. The temperature of furnace was 800°C at the time of lowering the crucible. Argon gas was passed at the rate of 4 cc per second using a silica tube. Argon flow was maintained throughout the duration of the experiment except for a few minutes when samples were drawn in a quartz tube using an aspirator. The furnace was maintained at the required

temperature for the specified duration of time before it was allowed to cool. The silica tube was flushed with argon gas for a few seconds before it was lowered into the melt to draw samples. The samples were taken both during heating and cooling cycles of the melt. Samples were subjected to sulphur and manganese determination.

3.3.3 Melting in Raising Hearth Furnace

Graphite crucible containing metal and additives was covered using a graphite lid. It was then placed in another refractory crucible which in turn was covered by a refractory lid. The assembly was heated to the desired temperature in the Molybdenum Disilicide furnace and maintained there for certain period of time. It was allowed to cool in a pre-determined fashion. The crucible was removed from the furnace when the temperature reached 1000°C. The solidified metal was recovered by breaking open the graphite crucible and it was subjected to chemical analysis.

3.4 Chemical Analysis of the Samples

3.4.1 Sample Preparation

The sample to be analysed was made slag free by grinding etc. It was powdered to size less than 0.15 mm using a pestle and mortar and 100 mesh sieve.

3.4.2 Manganese Determination

0.1 g of the powder sample was dissolved in 20 ml of 1:3 nitric acid and boiled for 1 - 2 minutes to expel oxides of nitrogen. The solution was then diluted to 60 ml. 5 - 10 ml of syrupy phosphoric acid and 0.5 g of potassium iodate were added. It was then boiled for one minute. The solution was cooled and made up to 100 ml in a volumetric flask. In case where manganese content was more than the instrumental analysis range, necessary dilution was made. The colour of the diluted solution was then matched against

standard samples of known manganese content. The wave length of 530 μ was used in the colorimeter analysis. The apparatus was calibrated using standard steel samples and cast iron samples of known manganese content.

3.4.3 Sulphur Determination

Sulphur was analysed using H_2S evolution technique in the laboratory. The set up was tested for any leakage of gas. This was done by pressurising the vessel with argon and noting any pressure drop of argon when supply of argon was cut-off. Leak test was also performed in a water tank to see any bubbling due to leakage of gas.

For analysing sulphur, 2.5 to 5 g of powdered sample was taken in a conical flask. Nearly 60 ml of ammoniacal $CdCl_2$ was added to the flask. The end of the glass tube was kept in this $CdCl_2$ solution. 150 ml of 1.1 HCl was poured drop by drop into the conical flask. Sulphur in the alloy reacted with HCl to form H_2S gas which was absorbed by ammoniacal $CdCl_2$ solution to form a yellow precipitate of cadmium sulphide. Towards the end of the reaction, heat supply was increased to produce steam and flush out the remaining H_2S in the flask. When it was confirmed that the gas has been completely flushed out, the solution was cooled in an ice bath. The ice cold solution was acidified with 20 ml of concentrated HCl solution. 10 cc of N/30 iodine solution was added to the solution and it was titrated against N/30 $Na_2S_2O_3$ solution using starch as an indicator. It was followed by titration of N/30 iodine solution alone with N/30 $Na_2S_2O_3$. Difference in the two values of $Na_2S_2O_3$ amount is the equivalent amount of $Na_2S_2O_3$ solution consumed for sulphur in the sample. The percent sulphur is given by:

$$[\%S] = \frac{0.016 \times 100 \times y}{z \times x}$$

where y is the amount of $Na_2S_2O_3$ consumed, z is the normality of the solution and x is the weight of sample in grams.

Chapter 4

THERMODYNAMIC MODEL FOR Fe-C-Mn-S SYSTEM

4.1 Method for Interpolation of Interaction Parameters

Melting point of iron decreases in presence of carbon. It may reach as low as 1150°C at around 4.5 pct Carbon. Most of the data for iron alloy are measured at 1600°C with reference to steel making conditions. It is necessary to know values of interaction parameters in the temperature range of 1200 to 1500°C in order to determine sulphur content in the carbon saturated metal. Pattjoshi [22] has developed a model for predicting values of interaction parameters by using regular solution model. For a regular solution, the quantity $RT \ln \gamma_i$ should not change with temperature. T is temperature in kelvin and γ_i activity coefficient of the solute in the Raultian scale. Raultian and Henrian interaction coefficient are defined as follows

$$\epsilon_i^J = \left(\frac{\partial^2 (\ln \gamma_i)}{\partial X_j \partial X_k} \right)_{X_i, X_j, X_k \rightarrow 0} \quad (4.1)$$

$$\epsilon_i^J = \left(\frac{\partial^2 (\log f_i)}{\partial (wt \% J) \partial (wt \% K)} \right)_{wt \% J, K \rightarrow 0} \quad (4.2)$$

As $RT \ln \gamma_i$ is constant for a regular solution, one can write the following:

$$RT_1 \varepsilon_i^j(1) = RT_2 \varepsilon_i^j(2) \quad (4.3)$$

Two types of interaction parameters are related by the following

$$\varepsilon_i^j = 230 \frac{M_j \varepsilon_i^j}{M_1} + \frac{M_1 - M_j}{M_1} \quad (4.4)$$

where M_j and M_1 are the molecular weight of solute j and solvent iron respectively Let

$$\frac{M_1 \cdot M_j}{M_1} = C_o \quad (4.5)$$

Combining equations (4.1), (4.4) and (.45) one may obtain the following.

$$\frac{1 - \left(\frac{C_o}{e_i^j(1)} \right)}{1 - \left[\frac{T_2 C_o}{T_1 e_i^j(1)} \right]} = \frac{T_1 e_i^j(1)}{T_2 e_i^j(2)} \quad (4.6)$$

By knowing the value of $e_i^j(1)$ at temperature T_1 , are can calculate value of e_i^j at any other temperature T_2 .

4.2 Thermodynamic Model

The various incoming and outgoing species are listed in Table 4.1 for the development of model equations

The following assumptions are made:

- 1 Added amounts of iron sulphide and manganese dissolve completely in iron alloy
- 2 Sulphur in the metal goes to the slag either as MnS or FeS
- 3 The equilibrium exists between slag and metal at the reaction temperature
4. The standard state for sulphur is taken as S_(4.35%C).
- 5 Elements such as silicon, phosphorous and carbon do not form any reaction products
6. Weight fraction of FeS and MnS are equal to their mole fraction
- 7 MnS and FeS in the slag form an ideal solution

Sulphur balance for the system gives the following equation:

$$Y_1 = \left[\frac{32.0 \times W_{FeS} / 88.0 + 0.01 \times (X_S \times W_{hm} - Y_2 \times Y_5)}{1 - Y_3 / 88} \right] \frac{87}{32} \quad (4.7)$$

Overall balance of the metal phase given the following:

$$Y_2 = W_{hm} + W_{FeS} + W_{Mn} - Y_1 \quad (4.8)$$

Manganese balance yields the following

$$Y_7 = 100 \left(\frac{(W_{hm} \cdot X_{Mn} \cdot 0.01 + W_{Mn})(100 - 0.61Y_1Y_4)}{Y_2} \right) \quad (4.9)$$

Slag-metal equilibrium may be represented by the followings:



Table 4 1 Lists of symbols used for material balance

Input

W_{FeS}	-	weight of FeS added
W_{Mn}	=	amount of Mn added
X_C	=	percentage of C in hot metal
X_{Si}	=	percentage of Si in hot metal
X_S	=	percentage sulphur in hot metal
X_P	=	percentage of P in hot metal
X_{Mn}	-	percentage of Mn in hot metal
X_{Fe}		percentage of Fe in hot metal
W_{hm}	-	amount of metal

Output

Y_1	-	amount of slag
Y_2	-	amount of metal
Y_3	-	weight fraction of FeS in the slag
Y_4	=	weight fraction of MnS in slag
Y_5	-	percentage of S in hot metal
Y_6		percentage of Si in hot metal
Y_7		percentage of Mn in hot metal
Y_8	-	percentage of P in hot metal
Y_9	-	percentage of Fe in hot metal
Y_{10}	=	carbon pick up.

$$\Delta G^o = - 6090.0 + 4.03 T \quad (4.11)$$

$$k_{FeS} = \frac{Y_3}{f_S Y_3} \quad (4.12)$$



$$\Delta G^o = - 39220.0 + 20.87 T \quad (4.14)$$

$$k_{MnS} = \frac{Y_4}{Y_7 Y_3 f_S f_{Mn}} \quad (4.15)$$

f_S and f_{Mn} in equations 4.12 and 4.15 respectively are calculated from the following equations

$$\log f_S = - \sum_{j=1}^N e_s^j (wt.\% j) \quad (4.16)$$

$$\log f_{Mn} = - \sum_{j=1}^N e_s^j (wt.\% j) \quad (4.17)$$

Here j stands for solute elements like C, Mn, S, P, Si. The value of e_s^j at different temperature can be calculated from the interpolating method given in Section 6. Computer programme was developed to solve the model equations. Details of the programme are given in the Appendix. Results of calculations are plotted to Figs. 4.1

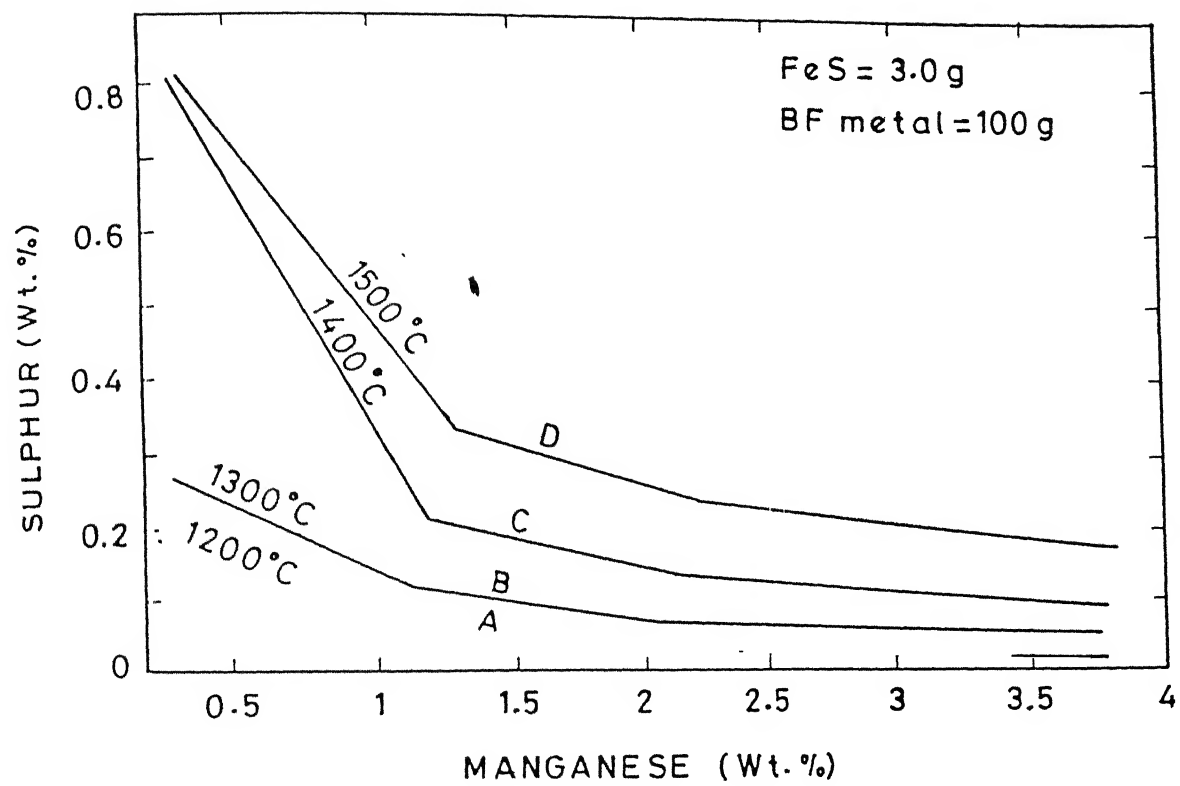


Figure 4.1: plot to show effect of manganese on calculated value of sulphur at different temperature.

CHAPTER 5

RESULTS AND DISCUSSION

Details of experiments carried out in the present study are included in Table 5.1. For experiments in category A and C, crucibles containing the required amount of metal and additives were slowly heated and held in the raising hearth furnace for 6h and 2h respectively at 1500°C and then allowed to cool in the furnace itself. For experiments in category B, thermal cycle consisted of the following

1. Heating the crucible in the furnace to 1500°C and holding there for 90 minutes
2. Cooling the crucible in the furnace to 1400°C and holding there for 120 minutes
3. Cooling the crucible in the furnace to room temperature

Experiments in category D and E were conducted in the silicon carbide furnace. Crucible containing the metal and additives was heated to the temperature beyond the melting range of the alloy and then allowed to cool in the furnace till the liquid metal resolidified. Samples were drawn from the melt at different temperatures both during heating and cooling cycles.

Results of sulphur determination in samples obtained from different experiments are summarised in Table 5.2. Sulphur contents of the standard sample was determined a number of times to check the reliability of the apparatus and the method used to analyse sulphur content of the metal. Results are summarised in Table 5.3. Determination of the sulphur content in the metal may be considered reliable because of the good agreement obtained between the experimentally determined values and the reported values for the standard sample. Experimentally determined manganese contents in these samples are plotted against estimated values in Fig 5.1. Because of the uncertainty in the analysis of manganese in metal samples in some experiments, manganese content of the sample was estimated by making the manganese balance.

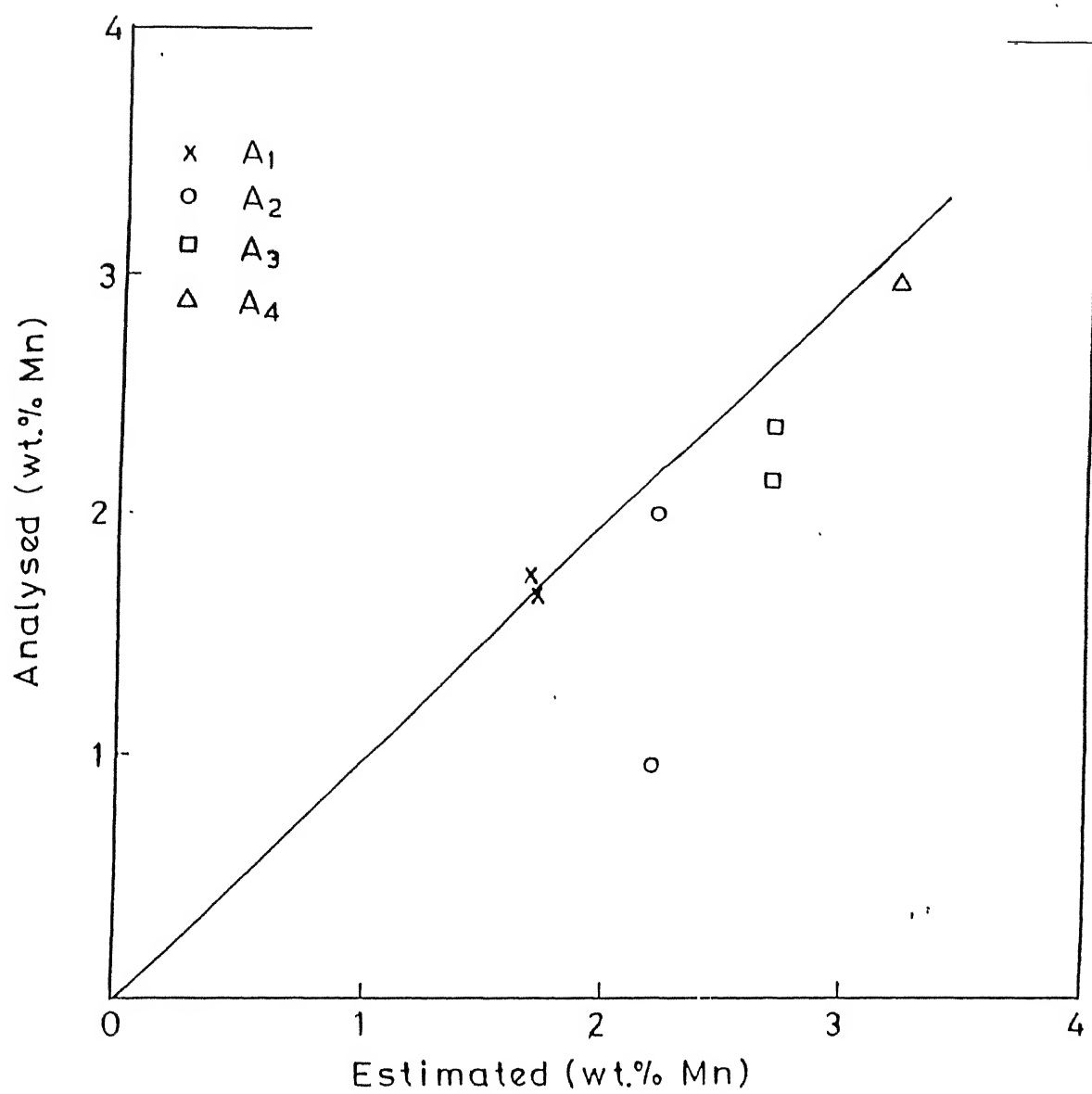


Figure 5.1: Analyzed manganese content of metal phase versus estimated manganese content for A category of experiments

For all experiments it was ensured that there was practically no slag adhering to metal sample before doing any analysis. It was possible to obtain slag free metal samples in a silica tube in experiments D₁ to D₃. For runs A₁ to A₄ and B₁ to B₃, slag free samples for analysis could be obtained by grinding the slag off the solidified metal. For runs C₁ to C₃, solidified slag layer was first removed by repeated hammering after breaking out the crucible. Clean and slag free metal for chemical analysis was obtained by further grinding off slag. For runs E₁ to E₃, enough care was taken to draw slag free samples from the liquid metal pool by ensuring that the end of the silica tube was beneath the slag level in the crucible. These samples were further machined using a grinder to make them completely free of any adhering slag layer.

Results show that for the experiment A₁ to A₄ and B₁ to B₃, sulphur content of metal decreased as manganese content increased. Results are plotted in Fig 5.2 and compared with theoretical predictions at different temperatures using model equations described in chapter 4. Measured sulphur contents are much less than the predicted values at 1500°C. However, measured values match well with the predicted values in the temperature range of 1200 -1300°C. One may conclude that there occurred a drop in sulphur during cooling of metal. As it took more than two hours for the liquid metal to solidify when left alone in the furnace, manganese could combine with sulphur to form manganese sulfide. This explains the results of most of experiments in category A and B. Limited number of experiments in category C on slag metal equilibrium highlight the following:

- 1 Sulphur content decreases with an increase in slag basicity i.e. CaO/SiO₂ ratio.
- 2 Sulphur content of metal is lowered by increasing the slag volume

From sulphur balance, one may show that sulphur content of metal is related to sulphur partition ratio as follows:

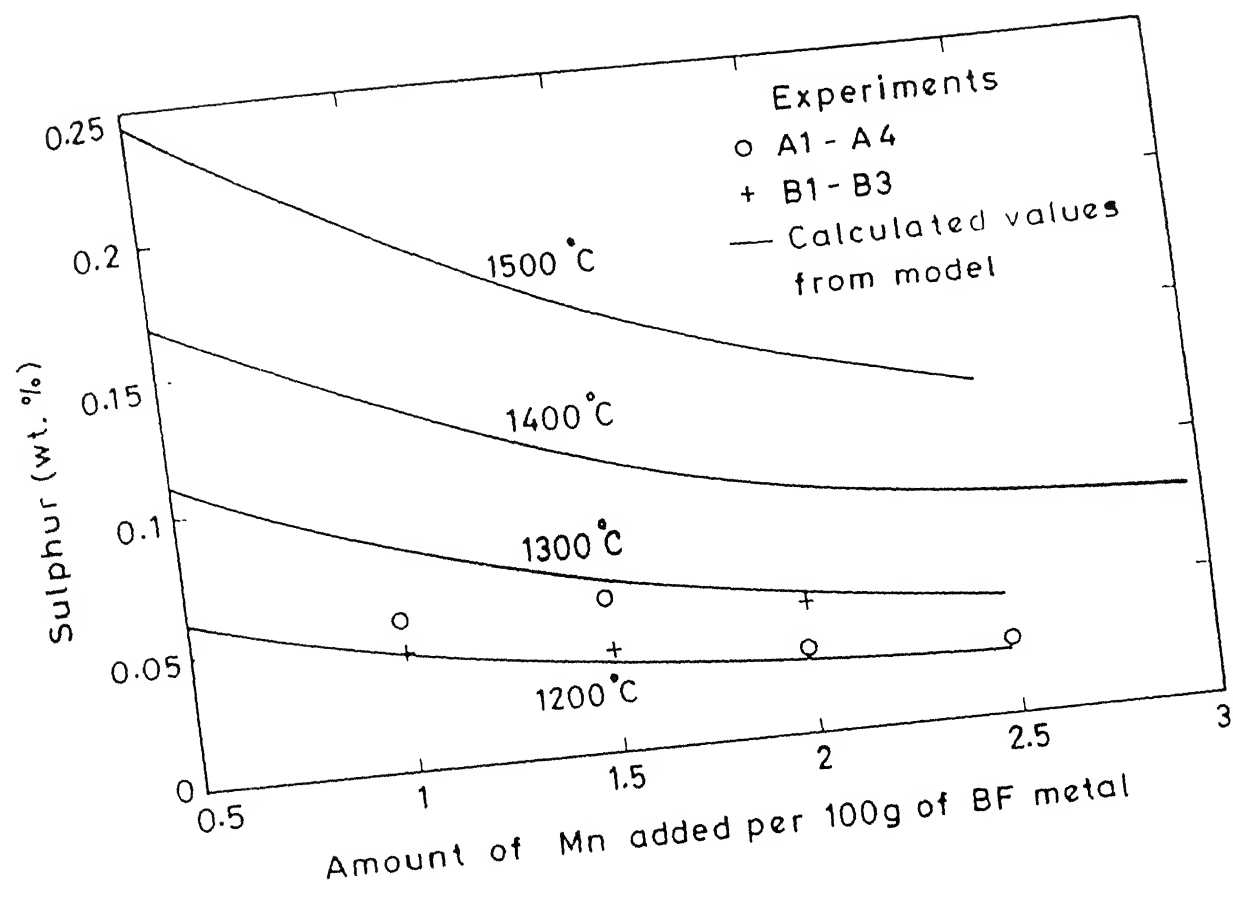


Figure 5.2: Plot to show change in sulphur content with manganese addition

$$[S] = \frac{(3200/88) (W_{FeS} / W_{BF}) + 0.04}{\alpha (W_{slag} / W_{BF}) + 1}$$

Sulphur content of blast furnace metal has been taken as 0.04 pct. From the results of experiment, calculated values of the sulphur partition ratio can be obtained and these are summarized in Table 5.4. Higher values of the sulphur partition ratio obtained at lower lime to silica ratio in experiment C₃ may be attributed to kinetic factors. Time taken by the metal to cool from 1500 to 1200°C is an important factor in presence of the manganese in such experiments. It confirms that both thermodynamic and kinetic factors are important to study to explain desulphurization of metal. For experiments D₁ and D₂, experimentally determined values and the values determined by using the model equations are plotted against temperature in Fig 5.3. There is good agreement between the two sets of sulphur contents of the metal. Results of experiment D₃ are also found to match well with the predicted values. For experiments E₁ and E₂, sulphur contents of the metal are compared with the predicted values from the model in Fig 5.4. Sulphur contents of the metal are found to lie in the range which is based on manganese sulphur equilibrium in the melt. This may be attributed to the fact that the slag was not playing any effective role in desulphurization as there was no stirring in the melt.

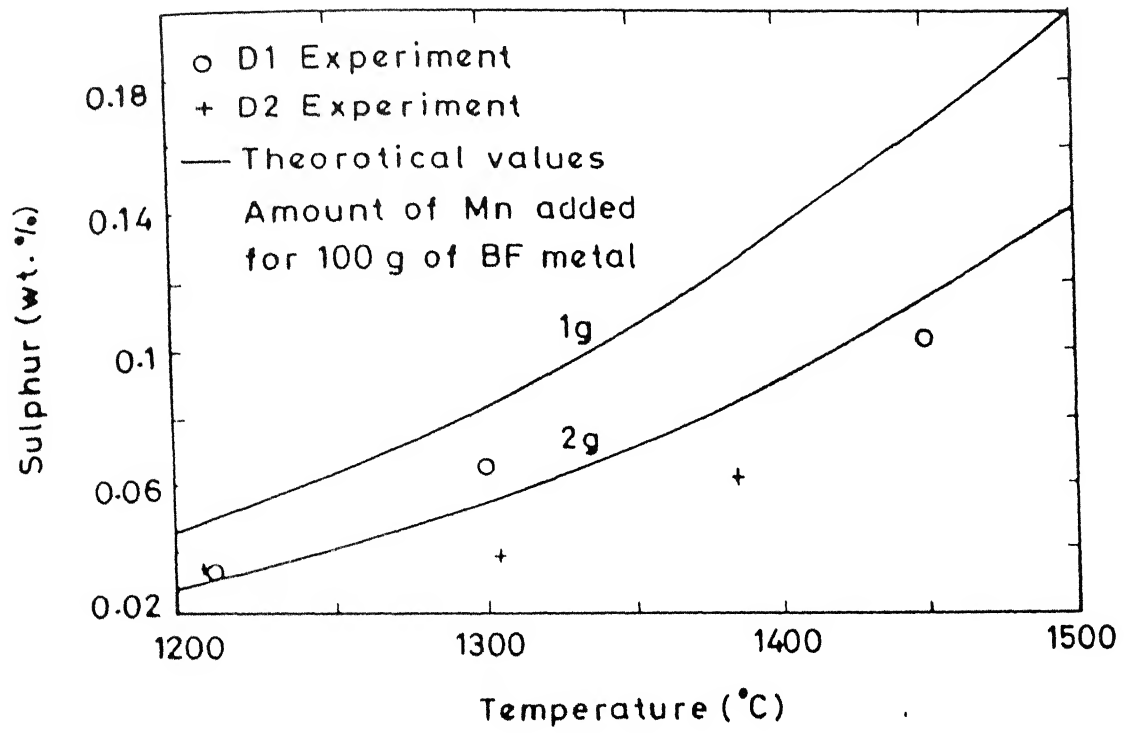


Figure 5.3: Plot to show change in equilibrium value of sulphur in the melt with temperature.

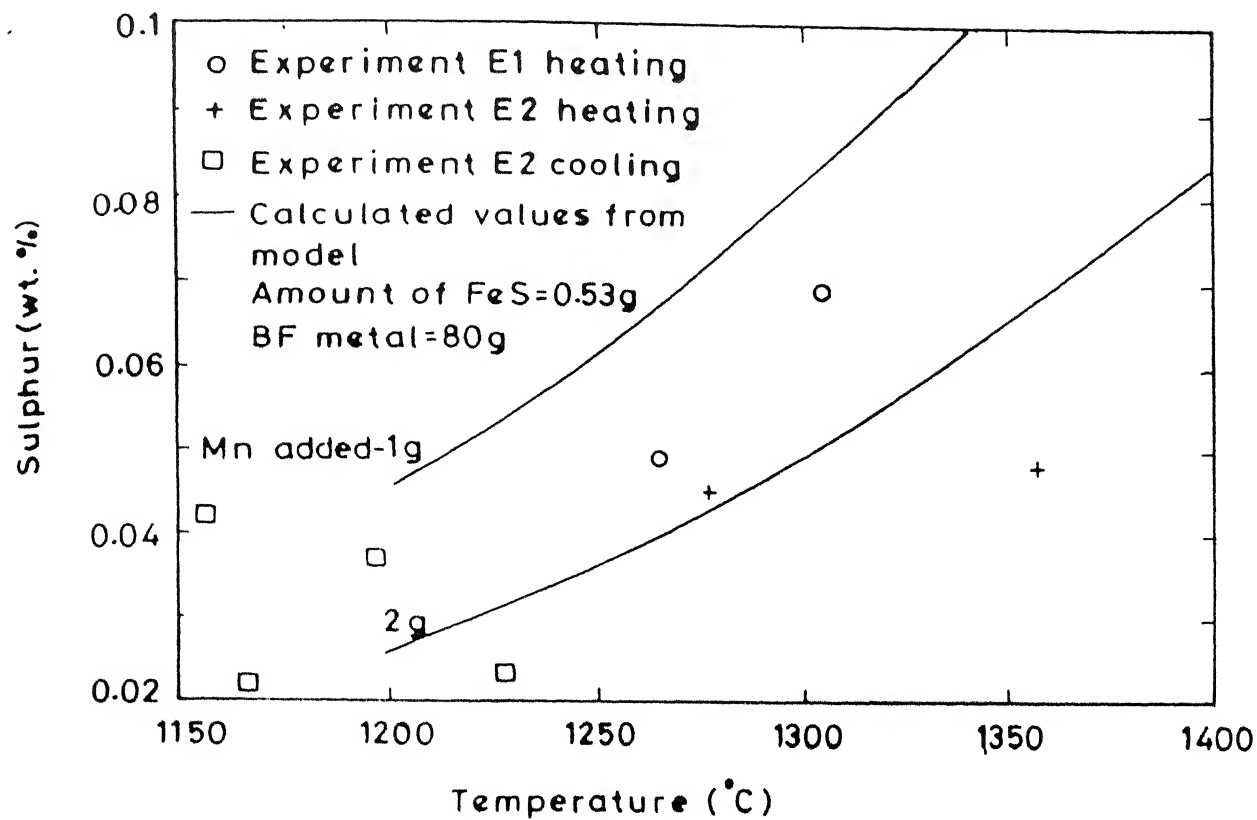


Figure 5.4: Plot to compare the sulphur content of the melt in experiments E1 and E2 with the value predicted by the model

TABLE 5.1

Details of Experiments Carried out in the Present work

Category	S N	BF Metal	FeS	Mn	CaO	Al ₂ O ₃	SiO ₂	Master Slag
		g	g	g	g	g	g	g
A	A ₁	100	0.277	1.043	-	-	-	-
A	A ₂	100	0.277	1.543	-	-	-	-
A	A ₃	100	0.277	2.001	-	-	-	-
A	A ₄	100	0.277	2.501	-	-	-	-
B	B ₁	100	0.277	1.049	-	-	-	-
B	B ₂	100	0.277	1.504	-	-	-	-
B	B ₃	100	0.277	2.014	-	-	-	-
C	C ₁	83	0.277	0	16	8	16	-
C	C ₂	83	0.277	0	17.5	8	14.5	-
C	C ₃	83	0.277	0	26.2	8	35.5	-
D	D ₁	100	0.377	1.005	-	-	-	-
D	D ₂	100	0.377	2.009	-	-	-	-
D	D ₃	100	0.754	6.009	-	-	-	-
E	E ₁	80	0.554	1	-	-	-	24
E	E ₂	80	0.554	2	4	-	-	20

TABLE 5.2

Results of Sulphur Determination in Metal Samples Collected

Experiment No	Temperature of Taking Sample oC	Sulphur Content	Sulphur Content	Sulphur Content
		I %	II %	(average) %
A ₁	*	0.058	-	0.058
A ₂	*	0.059	-	0.059
A ₃	*	0.034	-	0.034
A ₄	*	0.030	-	0.030
B ₁	*	0.045	-	0.045
B ₂	*	0.039	-	0.039
B ₃	*	0.050	-	0.050
C ₁	*	0.042	0.034	0.037
C ₂	*	0.035	0.030	0.033
C ₃	*	0.0168	0.0163	0.0165
D ₁	1212	0.034	-	0.034
D ₁	1301	0.065	0.073	0.069
D ₁	1450	0.104	-	0.104
D ₁	*	0.0448	-	0.0448
D ₂	1208	0.035	-	0.035
D ₂	1304	0.035	0.041	0.038
D ₂	1385	0.062	-	0.062
D ₁	1212	0.034	-	0.034
D ₁	1301	0.065	0.073	0.069
D ₁	1450	0.104	-	0.104

Table 5.2 Continued

D ₂	1208	0.035	-	0.035
D ₂	1304	0.035	0.041	0.038
D ₂	1385	0.062	-	0.062
D ₂	*	0.040	-	0.040
D ₃	1250	0.0362	-	0.0362
D ₃	1300	0.0373	-	0.0373
D ₃	1350	0.049	-	0.049
D ₃	*	0.033	-	0.033
E ₁	1265	0.049	-	0.049
E ₁	1305	0.069	-	0.069
E ₁	*	0.0560	-	0.056
E ₂	1277	0.0448	-	0.0448
E ₂	1357	0.048	-	0.048
E ₂	1227	0.023	-	0.023
E ₂	1197	0.037	-	0.037
E ₂	1167	0.022	-	0.022
E ₂	1157	0.042	-	0.042

* Solidified metal in the crucible after the experiment.

TABLE 5.3
Results of Analysis of Standard Cat Iron Sample

S.N.	Sulphur %
1	0.0533
2	0.0629
3	0.052
4	0.0607
5	0.062
6	0.064
Average	0.059
Reported	0.067

TABLE 5.4

Results of Calculations of Sulphur Partition Ratio

Experiment No	CaO/SiO ₂ ratio	W _{FeS} /W _{BF} Ratio	S _{slag} /W _{BF} Ratio	Sulphur Content %	Partition Ratio
C1	1.0	0.00335	0.48	0.027	4.8
C2	1.2	0.00335	0.48	0.035	5.2
C2	1.20	0.00335	0.48	0.030	6.4
C3	0.73	0.00335	0.94	0.0163	6.9
C3	0.73	0.00335	0.94	0.0168	6.6

CHAPTER 6

SUMMARY AND CONCLUSION

- (1) Model equations based on materials balance and slag metal equilibrium have been developed and solved using a computer programme to determine sulphur content of the metal phase due to additions of different proportions of iron sulphide and manganese metal to blast furnace iron at different temperatures of the bath
- (2) Results of model calculations show that sulphur content of metal decreases with an increase in manganese content of the bath at constant temperature. Results also reveal that sulphur content tends to fall with lowering of metal temperature at constant manganese content of the metal.
- (3) One silicon carbide tube furnace has been designed and constructed in the laboratory to reach 1400°C. Its temperature can be controlled within $\pm 2^\circ\text{C}$. Samples of bath can be drawn during heating and cooling stages. Results of sulphur analysis of the samples agreed well with the predicted results using the model equations.
- (4) Some experiments were carried out by addition of manganese as well as slag but without any stirring of the bath. Results showed that sulphur content did not fall beyond the levels predicted by the manganese sulphur interactions.
- (5) Some experiments were carried out using the raising hearth type furnace at 1400 and 1500°C. Samples could not be taken during the experiment duration. Sulphur content of the solidified metal in the crucible after the experiment agreed with the model results at 1200 and 1300°C and not at 1400 and 1500°C. It shows that considerable drop in sulphur occurred during cooling stages even without stirring of the bath.

- (6) Practical importance of the study lies in the observed drop in sulphur content of hot metal in the ladle during its transport from the blast furnace to mixer stage in the steelmaking shop whenever the manganese content of metal exceeded 1 pct. Further drop in sulphur may be envisaged if slag is added to decrease the activity of manganese sulphide but this may require extensive stirring of the bath.

References

- [1] C. W. Sherman and J. Chipman; *trans. AIME (J. of Metals)*, pg 957, June (1952)
- [2] Ban-Ya and J. Chipman, *Trans AIME*, 242 (May 1960), pg 940
- [3] J.P. Morris and R.C. Buhel; *Trans. AIME* (1950), 188, pg 317
- [4] C.J.B. Finchman and F.D. Richardson; *Proc. R Soc. A*, 233 (1954), 40; *J. Iron. Steel Inst*, 178 (1954), 4.
- [5] A.S. Venkatrathi and H.B. Bell; *JISI*, (Aug, 1969), vol. 207, 1110
- [6] M.R. Kalyanram; *ibid*, 1960, 195, 68
- [7] Kim Karsiad; *Scandinavian Journal Of Metallurgy*, 1984, 13, pp. 140-150
- [8] E.T. Turkdogan; *Physical chemistry of high temperature technology*; Academic Press (London), 1980, 359-364
- [9] Ed. S.S. Gupta and Amit Chatterjee, *Blast furnace iron making*; Tata Steel; 1991, pp 135-138
- [10] T.B. King and S. Ramachandran; *Physical Chemistry of steel making*; Ed. J.F. Elliott, John Wiley, New York, (1958)
- [11] Fulton J.B and J. Chipman; *Physical chemistry of steel making*; 1958; Chapman and Hall; pp. 113-116
- [12] Yasujim Kawai and Katsumi Mori; *Trans. ISIJ*, 1973, vol. 113, pp 303-317

- [13] Frohberg and M L Kapoor ; *Proceeding ICSTIS, Trans. ISIJ*, 1971, 11, pp.495-500.
- [14] Craig F Landefeld , *Proceeding 5 th Iron and steel Congress*,1981,Whashington D C , pp 429 -439
- [15] G.A Iron and R.I.L. Guthrie; *Ironmaking and Steelmaking*, 1981 ,No.3, pp 114-120.
- [16] L K Chiang, G A. Iron, W.K. Lu ; *Proceeding of 5th iron and steel congress* ,1986, Whashington. pp 441-451
- [17] Tabala, *Trans AFS* ,1976 ,122, pp. 775-786
- [18] L K Chuang etal; *Iron and Steelmaker*,Jan1990 , pp. 35-52
- [19] W Oelsen, *Stahl und Eisen*,1948,131,pp. 175 -186
- [20] J P Morris, *Journal of Metals*(September1952),pp. 939 – 940
- [21] N J. Grant etal; *Trans. AIME,Journal of Metals (Nov.1953)*,pp. 1451 – 1454
- [22] A.K. Pattjoshi; *Ph.D Thesis*, I I.T.,Kanpur (1984)
- [23] E T. Turkdogan, *Metalurgical Transaction* , June 1978 , 9B , pp. 163 – 179
- [24] R.H Rem and J. Chipman; *Trans. TMS - AIME* , 1965, vol 233, pp.415 – 25
- [25] K.P. Abraham; *Journal of iron and steel institute*, 1960, vol 196, pp.82 – 89
- [26] E.T. Turkdogan; *Iron making steel making* , 1980, 9, 268
- [27] Biswas , A.K *Principal of blast furnace Iron making*, 1981, SBA Publ.

COMPUTER PROGRAMME TO SOLVE MODEL EQUATIONS IN Fe-C-Mn-S SYSTEM

```

real k1,k2,wfes,xc,xsi,xs,xmn,t,r,eps,yfes,ymns,yfe,yc,ycc,whm
real ycpick,ycl,tl,ar,br,a,b,fs,fmn,at,fein,feout,ymetal
real wmn,xfe,yslag,tc,ymn,ysi,yp,error,yss,xp,ys
open(20,file='in.dat')
open(21,file='out1.dat')
open(22,file='out2.dat')
wfes=0.5535
whm=80.
wmn=2.0
xc=4.3
xsi=0.5
xs=0.05
xp=0.25
xmn=0.7
t=1200
r=1.987
eps=0.001
read(20,*) wfes,whm,wmn,xc,xsi,xs,xp,xmn,t,r,eps
write(22,223)
223 format(25x,'%C      %Si      %P      %Mn      %S      Temp. C error'//)
write(21,225)
225 format(25x,'metal      slag      Fes      Mns'//)
do i=1,7
t=1200+50*(i-1)
xfe=100.-xc-xsi-xp-xmn-xs
tl=t+273.
a=(-31580.0/(r*tl))+19.61/r)
k1=exp(-a)
b=(1550.0/(r*tl))+2.63/r)
k2=exp(-b)
ar=1.34+2.54*0.001*t
br=0.04*xmn-0.35*xp-0.4*xs-0.3*xs
ycl=ar+br
yc=ycl
ys=xs
ymetal=whm+wfes+wmn
fs=7.0
fmn=0.8
102 ycpick=(ymetal*yc-xc*whm)*0.01
101 yfes=ys*k2*fs
if(yfes.le.1.0) go to 222
yfes=1.0
ys=1.0/(k2*fs)
222 ymns=1-yfes
at=(32.0*wfes/88.0+0.01*(xs*whm-ymetal*ys))*(87./32.)
yslag=at/(1.0-0.0042*yfes)
ymn=100.*(wmn+0.01*xmn*whm-(55./87.)*ymns*yslag)
/ymetal
yss=ymns/(ymn*k1*fmn*fs)
if(abs(yss-ys).le.eps)goto 100
ys=yss
gotol01
100 ys=yss
ysi=(xsi*whm)/ymetal
yp=(xp*whm)/ymetal
tc=0.04*ymn-0.35*yp-0.4*ys-0.3*ysi

```



```

ycc=ar+tc
if(abs(ycc-yc).le.0.001)goto 106
yc=ycc
goto 102
106 yc=ycc
ymetal=whm+wmn+wfes+ycpick-yslag
fein=(56.*wfes)/88.+0.01*xfe*whm
yfe=100.-ymn-ysi-yp-yc
feout=0.01*ymetal*yfe+yslag*yfes*0.636
error=(feout-fein)*100.0/fein
c print *,ymn,yfe,ymns,yfes,yslag,ys,ymetal
write(21,221)ymetal,yslag,yfes,ymns
write(22,224)yc,ysi,yp,ymn,ys,t,error
221 format(/22x,4f7.2)
224 format(/22x,5f7.3,f7.1,f7.3)
enddo
stop
end

```

```

ycc=ar+tc
if(abs(ycc-yc).le.0.001)goto 106
yc=ycc
goto 102
106 yc=ycc
ymetal=whm+wmn+wfes+ycpick-yslag
fein=(56.*wfes)/88.+0.01*xfe*whm
yfe=100.-ymn-ysi-yp-yc
feout=0.01*ymetal*yfe+yslag*yfes*0.636
error=(feout-fein)*100.0/fein
c print *,ymn,yfe,ymns,yfes,yslag,ys,ymetal
write(21,221)ymetal,yslag,yfes,ymns
write(22,224)yc,ysi,yp,ymn,ys,t,error
221 format(/22x,4f7.2)
224 format(/22x,5f7.3,f7.1,f7.3)
enddo
stop
end

```



Date Slip

This book is to be returned on the
date last stamped.

[illegible]

MME-1998-M-DOB-ROL



A126864